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VOL. 43 NO. 397 JANUARY 1957

THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 3 October 1956, the Chair being taken by The Rt. Hon. Lord Geddes, President of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman, introducing the author of the paper to be presented, said: Mr Capdeville graduated from the Ecole Polytechnique, Paris, in 1926. After spending two years in the automobile industry with Citroen, in 1930 he entered the service of the French subsidiary of the then Anglo-Iranian Oil Company, where for nine years he held the post of Assistant to the Chief Engineer responsible for the technical problems of the distribution of petroleum products. After the war, he was sent by the French Government on a mission to the U.S.A. to study the economic and technical problems raised by pipelines for finished products. He was subsequently entrusted with the engineering studies of the Le Havre–Paris pipeline and, on the formation of the TRAPIL company, responsible for the construction and operation of that pipeline, he was appointed Operations Manager, a post which he holds at present.

Mr Capdeville is a member of the French Association of Petroleum Technicians, to whose work he contributes, and he has been a member of that association's committee.

The following paper was then presented in summary.

THE LE HAVRE–PARIS PIPELINE*

By J. B. CAPDEVILLE†

WHEN, after the second world war, France had to consider the reconstruction of her installations, crude oil refining plants, and distribution system, she strove to revise the ideas which had induced her to utilize machinery and equipment of one kind or another in the light of the most recent international developments. It was thus that she was led to consider the possibility of using long-distance pipelines. With the refineries located at seaports and that of BP at Courchelettes having to be reconstructed at Dunkirk, there was no problem in respect of a crude oil pipeline. On the other hand, surveys that were undertaken indicated that, for at least two regions, a pipeline for refined products was beneficial, namely, (1) from the refineries located in the Lower Seine area up to the Paris area because of the considerable demand in that region; (2) from the Marseilles refineries as far as Switzerland in consequence of the industrial importance of the Rhône valley.

The survey of this second pipeline has not advanced beyond the preliminary design stage.

France has always relied and continues to rely, although in a lesser degree, upon a very precise system of petroleum installations. The French Government which adopted the principle of electrifying the railways of the Rhône valley and of improving navigating conditions on the Rhône, considered that this pipeline project could overlap the investments already decided.

Therefore the construction of the Le Havre–Paris pipeline was undertaken and put into operation at the beginning of 1953.

As it was intended to operate the pipeline according to orders emanating from various companies, and as it would have the status of a common carrier, its construction and operation were undertaken by a joint economy company in which the French State holds a certain number of shares.

INTRODUCTION

For the survey, construction, and operation of this pipeline, it was necessary to take into account the structure and particular conditions required by the French petroleum industry, administrative regulations, and the equipment capable of being furnished by the national industry.

The diversity of the points of origin and delivery necessitated individualized deliveries to customers, that is to say they had to receive products with a guarantee of origin. It was also necessary to take into account French regulations concerning safety precautions, Customs, and weights and measures.

Finally, as there was a lack of foreign currency in France at the time of construction, it was necessary to utilize the resources of French manufacturers to the maximum; even though French industry has manufactured refining material for many years, it was not prepared to furnish specialized equipment for pipelines except after extensive research.

The problem was to connect the refineries of the Lower Seine area with all the depots of the Paris region. The latter were divided into geographical areas and, at the optimum point of the area, a terminal

* MS received 9 July 1956.

† Société des Transports Pétroliers par Pipe-line.

station was envisaged in order to supply the tank farms in this region—the terminal being connected by special pipes to the depots which it feeds.

The problem was rendered more complex, chiefly from the point of view of dispatching, because of the complications which would arise in keeping all the depots supplied. However, this complication was largely compensated for by the fact that existing depots could be utilized and, in consequence, the construction of new depots could be avoided. Deliveries by pipeline as close as possible to the points of highest consumption would therefore be assured, thus reducing the distances that road tank cars would have to cover.

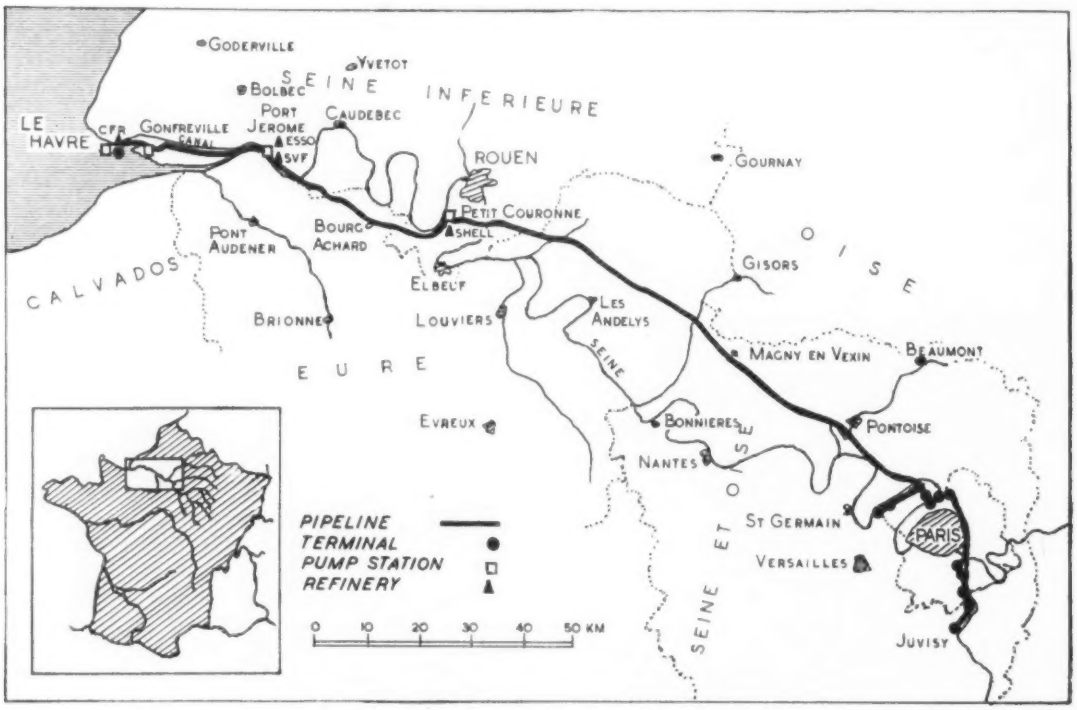

FIG 1
ROUTE OF THE LE HAVRE–PARIS PIPELINE

GENERAL DESCRIPTION AND CONSTRUCTION OF THE PIPELINE

A 10-inch-diameter pipe was selected in order to allow the transport of a maximum of about 2,200,000 metric tons/year.

The pipeline was constructed partly with grade B, API seamless pipe, and partly with grade C, API seamless pipe, recovered from a military pipeline.

Modern methods of construction were employed, and they consisted chiefly of: (1) adopting a route as straight as possible in traversing open country, with a view to reducing the overall length of the pipeline and thereby its cost price; (2) breaking up the pipe-laying with specialized gangs working at the same speed and provided with appropriate mechanized equipment; (3) executing the welding by several gangs, the speed of the welding, in fact, determining the overall progress of the line.

The protection of the pipe against external corrosion was obtained by a special coating of insulating material and by cathodic protection.

This coating, in conformity with the most recent American specifications, consists of a layer of primer and one of bituminous enamel, reinforced by layers of fibreglass. This renders it rot-proof and, at the same time, ensures an insulation above 10,000 ohms/sq. cm. (10,000–15,000).

This insulation permits the realization of cathodic protection at a very low cost and without danger to neighbouring installations.

Five rectifier stations suffice to ensure the current drainage of the pipeline in rural areas. The total power absorbed by the five rectifiers is less than 200 watts.

The absence of stray currents has permitted the utilization of drainage stations in the whole rural area; these stations consist essentially of a transformer and a rectifier, the negative pole of the recti-

fier being connected to the pipeline, whilst the positive pole is grounded, thereby forming an anode whose function is to discharge the current drained from the pipeline into the ground. The evolution of the potentials of the conduit has been, and will continue to be, carefully attended to. The situation appears to have been stabilized, and periodic checks will permit future modifications in regulating conditions.

In the Paris region, the problem was more complex for two reasons, first, the existence of stray currents originating from electrified rail tracks, and secondly,

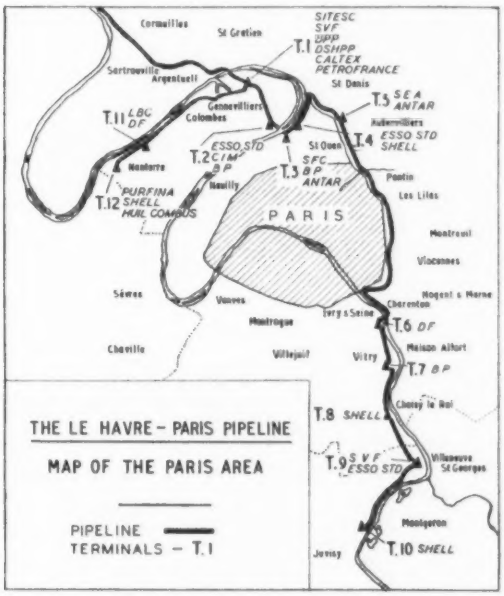

FIG 2

the existence of numerous underground structures, susceptible to damage by the cathodic protection of the pipeline, which, therefore, required to be very precisely determined.

The system adopted was that of a cathodic drain unit, and such a device has been installed near Paris. The principle of the device is that it must be connected electrically to the pipeline and to a nearby railway track, the rail replacing the ground connexion of the drainage station. The variations during the day in rail tension having been previously closely studied, the cathodic protection equipment is then installed. It suffices therefore to provide relays automatically permitting the rectifier to come into operation or not, according to whether the rail has a negative or positive potential. In this way, the exchange of current is always from the pipeline to ground; an exchange realized without the rectifier when the rail itself is negative. This device has given every satisfaction.

Finally, potential take-off points have been installed from place to place along the pipeline. They permit the calculation of the average value of electric insulation of the coating by very simple methods. These measures, carried out periodically, ensure a close survey of the evolution of this insulating value.

FIG 3

VIEW OF ONE OF THE PUMPING STATIONS

If it dropped too low, the pipe would be unearthed and the coating renewed, thus ensuring perfect protection of the steel.

The major factor in the cost price of transportation by pipeline lies in the duration of life of the tubes, and no precaution which eliminates all risk of corrosion is excessive.

TECHNICAL CHARACTERISTICS

With a view to reducing the number of pumping stations to a minimum, it is in our interest to carry out pumping at maximum pressure compatible with the resistance of the line. Maximum pressure reached 70 kg/sq. cm.

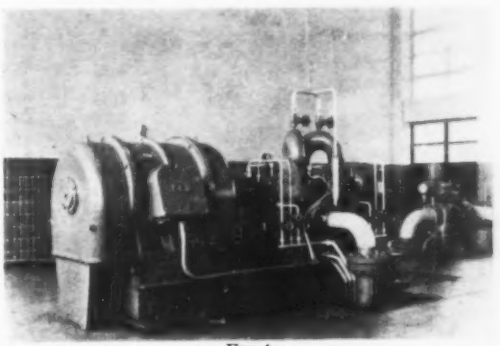

FIG 4

A PUMPING GROUP CONSISTING OF THE ELECTRIC MOTOR, WITH EXTRA REINFORCEMENT, AND THE THREE-STAGE CENTRIFUGAL PUMP

Pumping stations are equipped with three- or four-stage centrifugal pumps which are capable of ensuring a throughput of about 450 cu. m/hr under a pressure of about 25 kg/sq. cm.

These pumps are fitted with mechanical seals which have given remarkable results.

They are driven by asynchronized electric motors

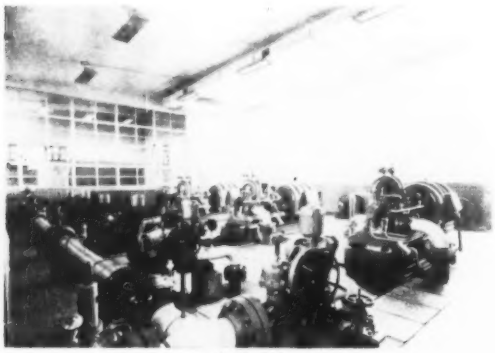

FIG 5 (*a*)

INTERIOR OF PUMPING ROOM

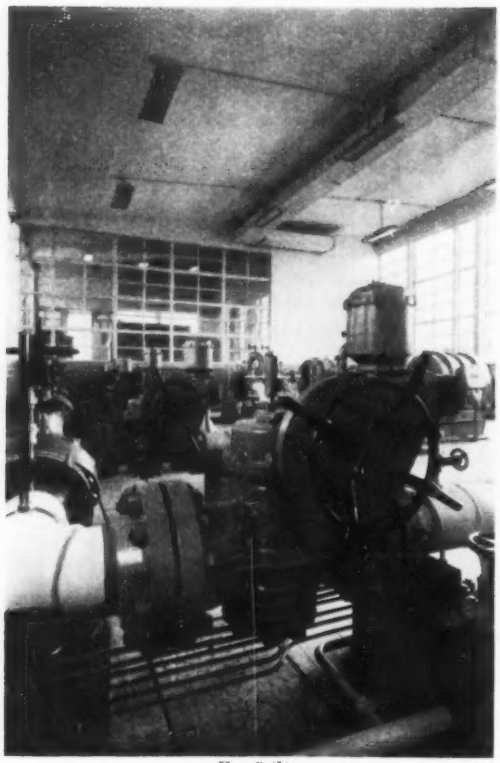

FIG 5 (*b*)

CLOSE-UP OF THE PUMPING ROOM INTERIOR

of 300 h.p. under voltage of 3000 volts, giving a speed of 2950 rev/min. They are not anti-explosive but are simply analogous to the "explosion-proof" type American motors with a larger air-gap and limited temperature range in windings. With a view to facilitating access to the various apparatus in the pump room, no fireguard walls were installed as are sometimes found in similar installations. To avoid all danger, the air ventilating the engines has no contact whatsoever with the air in the pump room, since having been filtered it is sucked in and evacuated outside the premises by a system of ventilating cowls situated below the flooring pavement of the room.

Naturally, the electrical installation is very complex, since it has to ensure not only the working of the engine but also numerous accessories, from motorized valves to ventilation, as well as relays to automatic controls, including safety devices. Material was used which appeared to be the simplest to handle so as to ensure the functional security of such items as circuit-breakers in small volume of oil, and the air-break switch with electromagnetic blow-out, for the starting of electric motors by auto-transformers.

Finally, the relays were enclosed in airtight boxes to protect them from dust. All these precautions have reduced initial operation starting difficulties and breakdowns to a minimum.

In view of the complicated operations at the stations and also of the lack of experienced personnel for operating the pipeline, automatic controls were extensively adopted.

The starting-up of the pumps and the bringing them into circuit are entirely automatic.

By pressing a single button, the operator sets in motion the following process: (1) the motorized valve at the intake side of the pump starts to open and is fully open in 90 seconds; (2) when the intake valve is completely open, the motors begin to work by auto-transformer under power of 2000 volts, this phase of the operation taking 20 seconds; (3) when the motor is working normally at 3000 volts, the outlet valve starts to open and is fully open within 90 seconds.

To stop the pumps, a push-button arrangement automatically brings a reverse action into play.

Safety Precautions

In connexion with safety precautions it is necessary to distinguish between:

(1) *Mechanical Security.* In addition to the classic safety precautions for electrical machinery, thermo-electric devices attached to the casing of the pump and on the bearings of the motors act as alerts in the case of any abnormal rise in temperature.

(2) *Hydraulic Security.* The following precautions have been envisaged: first, automatic regulator valves maintain at predetermined values the suction and discharge pressures at each pump station; secondly, in the case of abnormal running conditions (*e.g.* too low a suction or too high a discharge pressure), mercoids automatically stop the motors that run the pumps.

(3) *General Security.* Rules and regulations govern-

ing the construction of petroleum storage depots have been strictly complied with.

Other Arrangements

Apart from this, other particular arrangements have been envisaged such as: drastic ventilation of the pump rooms, where the atmosphere is changed twenty times every hour; maintenance of atmospheric depression in the pump rooms, by which hydrocarbon vapours are excluded from penetrating the control room, together with an automatic alarm when the

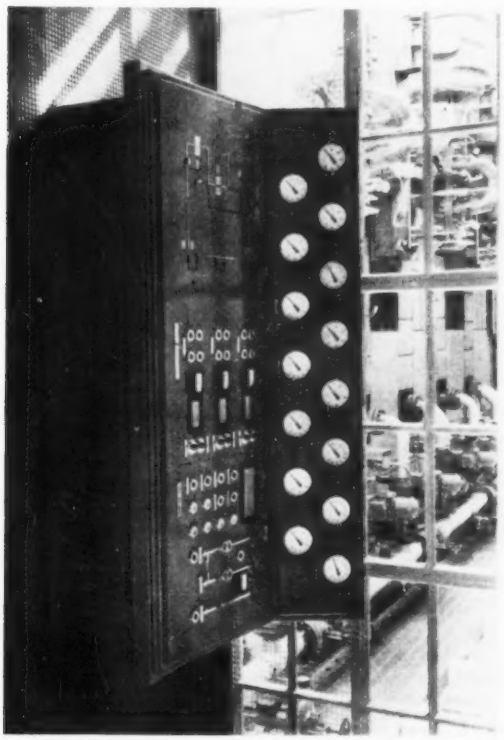

FIG 6

CONTROL PANEL OF A PUMPING STATION

predetermined value in the differential pressure is unrealized; permanent control of the amount of inflammable vapour in the atmosphere of the pump rooms with an automatic alarm system which is brought into action when the dangerous predetermined level is exceeded; control of differential pressure between the intake and outlet on the filters in order to detect clogging, which is alerted by an automatic alarm; in a general way, all abnormal conditions are signalled by the illumination of a bulb on which is fixed a micro-film which indicates the defect by projecting it on to frosted glass situated on the desk of the control board. This facilitates the work of the operator.

Additionally, transport requirements are such that it was necessary to construct two intermediate stations which function only in winter to meet offtake of oils used for central heating.

As these stations function intermittently, their operation raised the problem of whole-time personnel. They are remote-controlled by the dispatching department, which controls the starting and stopping of its motors and receives automatically all information regarding its hydraulic functioning (pressure and flow rate). The department is also provided with a sighting board concerning the mechanical functioning (temperature of bearings, winding, transported products, etc.).

Operational requirements raise the question of precise measuring of products. Actually, the pipeline is committed to deliver in the Paris region the exact quantities of products it has received at the outset, and all errors must be avoided in measuring these quantities, as they can lead to serious financial charges. This problem has been solved by the use of volumetric meters whose installation and function are surveyed in detail later.

Before finishing with the description of the technical installations in the stations, it is necessary to indicate that the conception of the buildings includes the following characteristics: (1) the lighting of the pump rooms is achieved by the extensive use of large bay-windows in reinforced concrete. The rooms are covered by a roof in reinforced concrete prolongated by an open shed 14·30 metres long composed of hyperbolic paraboloid with stretchers. Thus, the zone in which is installed the complex system of pipes, decanters, filters, counters, valves, and security appliances, sheltered by the open shed, is independent of all points of support; (2) all channels and ventilating cowls are placed in close culverts either in the interior of the room or under the open shed in such a way as to facilitate the movements of the personnel; (3) with a view to respecting safety regulations, an important consideration was a logical lay-out which would not hamper easy access or operations; (4) a certain æsthetic consideration was devoted to the lay-out, not only in the conception of the buildings themselves, but also to the colouring of the working areas and the provision of lawns, so that personnel would have an attractive working site that, in turn, would encourage them towards the careful maintenance of all mechanical accessories.

Compared with the stations, the terminals are much more simple. They are constituted by a measuring manifold, where products are filtered and measured by meters, and a distribution manifold, which assures the switching of batches towards depots with which they are connected.

The terminals at the extremities are more complicated and consist chiefly of scraper traps, water decanters, and 140 cu. m. tanks, because contaminated products, of which more will be said later, are directed towards these points.

The receiving terminal in the Paris region is also more complicated, since it has to ensure the switching

of products towards the Western and Southern spreads.

OPERATIONAL CHARACTERISTICS

The Le Havre–Paris pipeline currently transports aviation petrol; jet fuel; ordinary motor spirit; high-grade motor spirit; diesel fuel; kerosine; and heating fuel.

With effect from the winter of 1956–57, the pipeline will also transport light fuel oil.

The product to be transported is taken from tanks at the refining source and is pumped up to the station on the main pipeline. This station then pumps the product to the Paris region with the aid of intermediate stations. As soon as a batch consigned to a particular depot arrives at the terminal to which it is connected within the Paris region, the terminal which was making deliveries just previously is stopped, whilst the valves on the second are opened. Personnel are only required on operating terminals, and this fact permits of a reduction in operational staff.

As related elsewhere, the pipeline is obliged to deliver batches to the same specification as those committed at the point of origin. It is therefore necessary to take all precautions to control the quality and quantity of batches.

As a result, the problem of quantity control is one of accurate measuring, and this is carried out by meters whose functions are more particularly described later.

In connexion with the guarantee of quality, the problem lies in the contamination which occurs between two products. When two different products follow one another in a pipeline a more or less important intermixture occurs at their point of contact. From research and experiments conducted on this

FIG 7

GENERAL VIEW OF A TERMINAL IN THE PARIS AREA

account, it is known that, under turbulent flow, contamination does not depend on the linear speed of the fluid when this is big enough (Reynolds No. above 15,000); increases in proportion to the difference in viscosity of the fluids in contact; and occurs, above all, at the start of the operation in the line. The contamination per unit length of distance covered is as proportionately low as the distance required to be run is high. If the distance to be covered is in excess

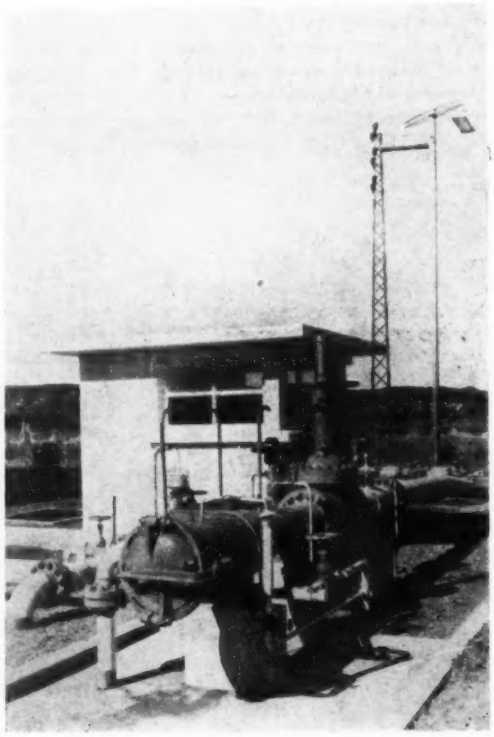

FIG 8

SCRAPER TRAP

of 10 to 100 (10 times higher) multiplication by 3 gives contamination.

Several different formulæ have been proposed which take into account, accurately enough, the importance of this phenomenon.

In practice, in the survey and operation of the Le Havre–Paris pipeline, it was necessary to arrange the circuits in such a way that contamination did not increase during the passage of the products in the pipe lay-out of the pump rooms. Personnel had to be trained in the delicate operation of switching contaminated products in a station and cuts had to be made with the greatest precision before and after contamination at the arrival of products within the Paris region.

Tests were made on the pipeline with a view to determining the effect of continuous operation of the line, the effect of stopping contamination in the line, and the possible efficiency of scrapers or jellified products.

The results of these tests were rather deceptive. It should be added, however, that the quantity of

contaminated products returned to the refineries for re-treating is very small, about one in 1000 of each batch transported.

The operation of a pipeline involves a number of delicate actions which are beyond the scope of this paper. It will suffice to speak of the switching of batches which, as will be related farther on, is carried out by the dispatching department, who issue precise orders in this connexion. The timing of cuts between batches is fixed either by appraising of the different physical characteristics, or by the measuring of the quantities received and distributed.

If two consecutive batches are composed of products having different densities, it suffices to record the moment when density readings change. In such a case, an operator watches the density recordings and alerts a second operator in charge of the valves at the exact moment when the cut has to be made.

If consecutive batches in the line each have the same density, they can be coloured for differentiation. These different colours, spotted through the sample-taking device, allow of the switching as described previously. If they are all the same colour, a coloured product inserted with care between each batch at the point of dispatch is sufficient to ensure the logging of the progress of the batch by observing the arrival of the coloured plug at destination.

Additionally, the operator at the terminal depot may receive orders to make the cut at the moment when a predetermined volume of product has been delivered.

The Le Havre–Paris pipeline transports an important number of products (thirty-two in all) by individual batches, and these include three aviation fuels (115/145, 108/135, 100/130); two jet fuels (TRO and JPI); four premium gasolines from refineries; one imported premium gasoline (Dutch); one non-ethylized premium gasoline; four ordinary gasolines from refineries; three imported ordinary gasolines (Russian, Rumanian, Italian); two special ordinary gasolines; one kerosine for illumination; four gas oils from refineries; two special gas oils (low sulphur content); four heating oils from refineries; and one light fuel oil.

The preparatory work is of considerable importance. Orders, worked out one month in advance, are forwarded to "planning" several days before the start of the month in question. A monthly estimates statement is then prepared by the planning department within 48 hours, and takes into maximum account the delivery dates demanded by customers.

This monthly statement is only of approximate value; it is further broken down to a more precise weekly statement established by "planning" in agreement with customers several days before the commencement of each week. This weekly schedule is compulsory and has to be accepted by customers, who may not ask for any further modifications.

Two days before delivery date, a daily statement is prepared giving the exact moment of supply. Finally, a few hours before each delivery, customers are advised by telephone of the precise time of delivery.

With a view to ensuring a guarantee of the products supplied, it is essential that, in all these statements, batches having the same characteristics are grouped together in a sequence influencing their introduction into the pipeline.

The following sequence must be observed, beginning with the heaviest product: light fuel oil; heating oil; diesel oil; kerosine buffer; motor spirit; premium gasoline; aviation spirit; premium gasoline; motor spirit; kerosine buffer; diesel oil; heating oil; light fuel oil.

It is thus a simple matter to include in batches any intermixture of products with characteristics which do not risk destruction.

The intermixture of light fuel with heating oil is included in the fuel oil batch; that of heating oil with diesel fuel is included in the heating oil batch; that of motor spirit and premium gasoline is included

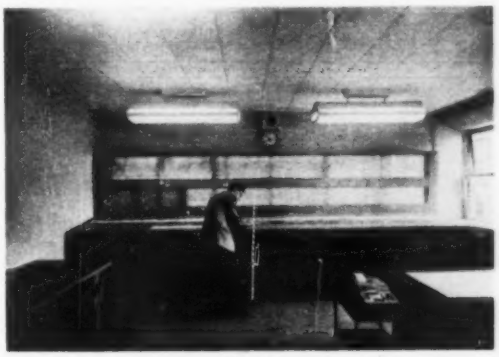

FIG 9

GENERAL VIEW OF THE DISPATCHING BOARD

in the motor spirit batch; and that of premium gasoline with aviation spirit is included in the premium gasoline batch.

Gas oil–kerosine and kerosine–gasoline intermixtures are, strictly speaking, contaminated. They are pushed to the end of the line and drawn into special tanks from where they are subsequently shipped by boat to the refinery for re-treatment.

The preparation of the dispatch programme is the responsibility of "planning"; its execution lies with "dispatching," which centralizes all relative information and passes on its instructions on the spot. This office, situated in the headquarters of the Company, is connected by direct telegraph and telephone lines to all installations.

The station and terminal chiefs must receive orders from the dispatching department in complete detail, because it is this department which alone has control of the overall problem. In this task it is largely aided by the positioning of the batches in the line, which it can follow because of a control board representing the line on a small scale. Consignments are represented by different bands of coloured paper according to the product and refinery of origin; these bands are

stuck together one after the other in such a way as to indicate the positioning of the batches. The complete band is placed in front of a fixed scale represent-

FIG 10

CLOSE-UP OF THE DISPATCHING BOARD, SHOWING PAPER TAPES REPRESENTING THE BATCHES

ing the pipeline with its pumping stations, as well as its delivery points. This band of paper is advanced along the scale each hour, according to the quantities taken off and delivered during the preceding hour in such a way that the dispatcher always has before him the position of the batches in the line at the preceding hour. To obtain greater precision it was necessary to bring all volumes down to 15° C. To take into account the fact that the line is not at 15° C, it was also necessary to correct the logging of the line in order to arrive at a fictional pipeline containing a volume at 15° C and not at its actual temperature. This correction is done by graduated verniers, because of which the logging of consignments is conveniently modified.

Due to these precautions, the precision achieved is excellent and forecasts of delivery times can be made to within a minute, on the average, without exceeding the maximum of three minutes.

It goes without saying that last minute changes are frequent as a result of operation incidents at refineries dispatching products and unforeseen modifications requested by receiving depots. The hazards involved in the timing of the turn-round of tankers must be equally taken into consideration. This is why it is so essential to adjust the weekly and daily programmes almost continually. This situation is further aggravated during the winter by increased transport demands, thereby obliging the pipeline to face continuous operation for several months. Seasonal fluctuations in offtake, however, permit the work of preventive maintenance to be carried out in the summer, thus considerably reducing the risk of breakdowns during the winter months.

PROBLEMS RELATING TO THE MEASURING OF PRODUCTS

The particular problem of measuring is one of the most difficult, and no solution, other than that of displacement meters, has been found. Measuring the intake into the line is the basis for the payment

FIG 11

VOLUMETRIC METER WITH TICKET PRINTER

to the refineries shipping products, and constitutes the taking-over by the pipeline; and measuring at the deliveries constitutes a discharge of responsibilities imposed on the pipeline. Both measuring operations, receipt and delivery, must be controlled by the Customs Department, as petroleum products are liable to taxation only at the deliveries from the depots.

As a result meters and the method employed to operate them must carry every guarantee of accuracy, and the meters must be acceptable to the Customs and Weights and Measures Departments.

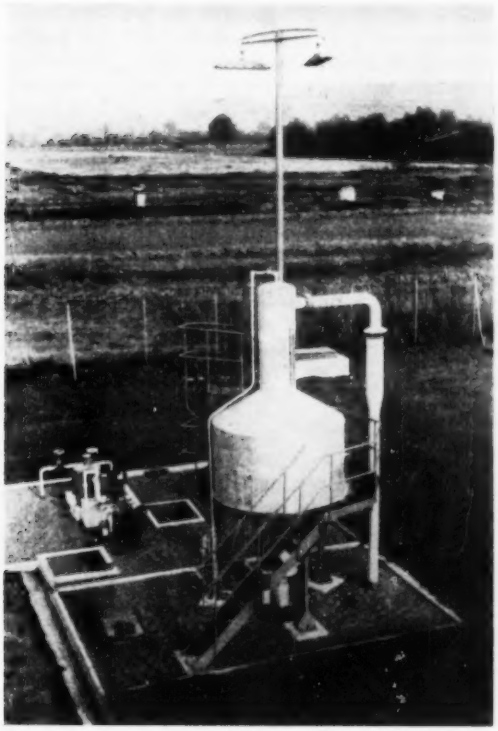

FIG 12

CALIBRATION TANK FOR THE TESTING OF VOLUMETRIC METERS

(1) *Description of the Installation of Meters*

The pipeline utilizes Pittsburg Equitable meters which are provided with ticket printers and are protected by microfilters which prevent deterioration by foreign matter. Installed in parallel, they can be operated in series by a calibrating meter.

(2) *Method of Measuring*

Each station is equipped with an insulated 1200-gallon calibration tank which contains three thermometers capable of recording correct internal temperatures. These calibration tanks are themselves calibrated by a 120-gallon master calibrating vessel of the Department of Weights and Measures to eliminate errors due to constructional differences that can exist between two calibration vessels. Controlling a meter by filling a calibration tank is a tedious and difficult task, since it causes the atmosphere of the tank to become saturated with gasoline vapour. A calibration meter was therefore envisaged which can be tested by comparison with the calibration tank. The correction coefficient of the calibration meter being known, the coefficients of the meters being used are obtained by putting each in series with the calibration meter. The average of two tests in each case is accepted, and these tests were repeated until the difference between them is less than 2·5 in 10,000.

The twelve terminal stations in the Paris region are not equipped with calibration tanks. A test station situated at a central point periodically undertakes the verification of calibration meters. This station, very carefully equipped, has four calibration tanks of 2400-, 500-, 50-, and 5-gallon capacities. They permit the testing of meters at various rates of flow and also the measuring of leakage rate. This station is utilized for the close control of all meters.

As an error of 1° C in measuring temperatures corresponds to an error of 0·1 per cent of the volume, correction of temperature readings is an equally necessary preoccupation. It is therefore essential to take temperatures at regular intervals, *e.g.* every 30 minutes, and, taking into account the quantities passed during each half hour, to establish a mean average temperature, which could then be applied to the entire consignment.

(3) *Meter Test Station*

The meter test station, referred to in the preceding paragraph, permits the calibration of meters situated in installations where there are no calibration tanks; the calibration of worn meters after overhaul; and the carrying-out of a complete series of general tests on the utilization of meters.

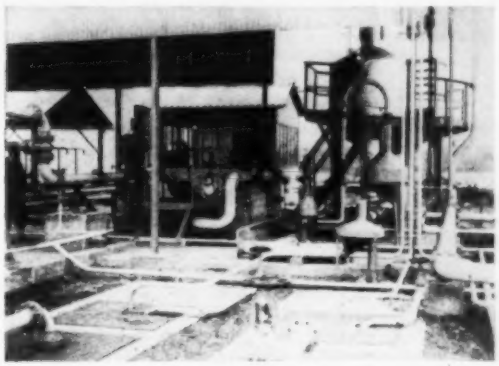

FIG 13

GENERAL VIEW OF THE VOLUMETRIC METER TESTING STATION

Provided with a complete set of calibration tanks from 5- to 2400-gallon capacity, this station has been equipped with great care with the following:

(*a*) a mechanism permitting the voluntary introduction of air for the study of the action of air and the efficiency of air separators;

(*b*) lay-out of line comparable to that of installations on the pipeline to eliminate all systematic errors caused by the design of the piping;

(*c*) pumps with variable flow rates for the study of the accuracy of meters on any throughput;

(*d*) regulating pressure valves for the study of the accuracy of meters in relation to products pressure;

(*e*) possibility of heating products for the study of the accuracy of meters in relation to the viscosity of products;

(*f*) special mechanisms to study the leakage rate which can, in certain cases, be considered as characteristic of the degree of deterioration.

(4) *Current Research*

In addition to current research with regard to the calibration of meters in service or after repairs, this station has conducted general tests which are directed chiefly towards the influence of the introduction of air in relation to the accuracy of meters for viscous products (diesel and heating oils); the influence of pressure on the accuracy of meters; and the influence of viscosity on the correction factor of meters.

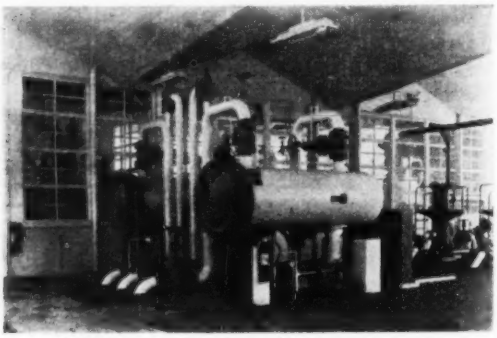

FIG 14

HAY TANKS WITH, ON THE EXTREME RIGHT, FILTERS FOR PROTECTION OF THE METERS

(5) *Results Obtained*

Excellent results have been obtained due to the mechanical quality and measuring methods of the meters, which, incidentally, are periodically dismantled for preventive maintenance. Their precision is excellent, and the products flowsheet for 1955 showed a balance between intakes and delivery of less than 0·08 per cent.

Recently, pressure correction has been added to temperature correction, and the accounts appear to have achieved equilibrium with an error of less than 0·03 per cent.

DESCRIPTION OF TESTS EFFECTED FOR THE TRANSPORT OF SPECIAL PRODUCTS

To illustrate the possibilities of pipeline transport, it is of interest to demonstrate how tests were conducted permitting the transport of special and delicate products such as aviation spirit, heating oils, and light fuel oils.

The principle of these tests is to ensure that the product to be transported does not suffer any modification to its characteristics in the course of its passage in the pipeline; that the mechanical equipment (pumps, filters, meters, etc.) is not affected; and that possible impurities contained in the products have no influence on the characteristics of the products following the batch under observation. Furthermore, these tests help to give an idea of the volume of contamination.

(1) *Pilot Unit*

A study on a pilot unit was undertaken before conducting transport tests on the pipeline itself. This unit consists of two circuits:

(*a*) *The principal circuit* (representing the pipeline), which comprises the following elements: five 50-litre tanks for the storage of different products requiring successive circulation; one metallic cloth filter; one hay filter; one pump of 4·5 cu. m/hr; one rotameter for measuring the flow; and one 1-inch tube, 5·5 metres long, representing the pipeline.

(*b*) *Secondary circuit:* permitting the cooling or heating of products and comprising one brine tank; one pump; and one cooling coil.

This equipment permits the successive circulation of different products in the 5·5-metre tube and also the examination of each product to see whether its characteristics underwent any modification in relation to the preceding product.

(2) *Aviation Spirit*

Tests on aviation spirit were, with exceptions, carried out in the pipeline itself without initial experimenting in the pilot unit.

The test consisted of the dispatch of a 1161 cu. m. batch of aviation spirit between two batches of motor spirit.

Special precautions were taken for the cleaning of filters, and for sampling, in containers thoroughly cleaned with detergents, at the intake and outlet of the pipeline.

Analysis revealed that the characteristics of products received were exactly the same as when they were dispatched, particularly the most sensitive characteristics, such as gum content and octane number.

(3) *Domestic Fuel*

Domestic fuel is a mixture of about 95 per cent gas oil with 5 per cent heavy oil.

A series of preliminary tests was made in the pilot unit, commencing with circulation of domestic fuel, followed by diesel fuel, and then followed by motor spirit.

These tests in the pilot unit led to the assumption that actual tests in the pipeline were possible. In fact, there was no variation in the density of domestic fuel, which appeared to have escaped any modifica-

tion. At the end of a period of rinsing which, extrapolated to the size of the actual pipeline, represented 1000 cu. m., the diesel fuel that followed recovered all its characteristics and, particularly, its colour, while the gum content of motor spirit which followed the gas oil showed no change on analysis.

A test was then attempted in the pipeline itself with a batch of 1000 cu. m. of domestic fuel, preceded by 3700 cu. m. of gas oil and followed by a 500-cu. m. batch of heating oil and 4700 cu. m. of diesel fuel.

Special precautions were taken to obtain a continuous flow so as to avoid sedimentation of the products, and to choose the easiest circuit in the piping manifold of pumping stations and terminals.

The results were entirely successful, as the characteristics of domestic fuel remained unchanged; except for colour, the diesel fuel recovered all its initial characteristics 100 cu. m. after the batch of domestic fuel; the gas oil recovered its initial colour 200 cu. m. after the batch of domestic fuel; and the gum content of the batches of motor spirit following the gas oil showed no change on analysis.

After this preliminary test, others were conducted to define exact operational conditions. Since these tests, made at the end of 1954, domestic oil has therefore been transported in the pipeline.

(4) *Light Fuel Oil*

This is a fuel with the following characteristics:

Density at 15° C	0·897
Asphalt	2·03
Conradson Carbon	4·5
Viscosity at 20° C	27·4 cS

Tests were carried out under the same conditions as for domestic fuel, in the pilot unit as well as in the pipeline. In this case also the experiments were successful, thus opening up the possibility of transporting this product during the winter of 1956–57.

These tests have also helped to decide the construction of a second pipeline which will be reserved for the transport of diesel fuel, heating oil, and light fuel.

CONCLUSIONS

The great possibilities in the transport of refined products by pipeline have been amply demonstrated.

The pipeline has shown itself capable of being adapted to a relatively complex structure of distribution in order to permit the supply of a large number of depots with individual batches ranging from aviation spirit to light fuel oil. Its operational flexibility is such that adjustments can be made from day to day against orders and stocks, factors that have been greatly appreciated during critical periods when other modes of transport have been dislocated by floods or ice.

In respect of quality and quantity guarantees, as well as accurate deliveries of batches, the pipeline has nothing to fear from similar services rendered to customers by other means of transport. Errors due to the line are very exceptional, and the great majority of customers have expressed themselves as being absolutely satisfied with services received.

In the effort that Europe will have to make to ensure the distribution of an ever-increasing tonnage of petroleum products, there is no doubt that the pipeline for refined products, as well as the pipeline for crude oil, will have an important part to play in the years to come.

DISCUSSION

S. D. Colwell: I should like to thank the author for his extremely lucid and interesting description of this fascinating operational development in petroleum distribution.

It is seen from the beginning of the paper that this pipeline was laid under what might be called government sponsorship, and that raises the question as to whether in addition to the obligations that must have been imposed on the pipeline company to act as a common carrier, the company were accorded certain corresponding rights, in the sense that the petroleum companies were themselves obliged by the Government to transfer a proportion of their requirements into the Paris region by pipeline. Was there in fact a guarantee of traffic, and were conventional methods not permitted?

Another point is that one assumes that if the pipeline company had in fact government powers, it was also able to exercise such powers in obtaining the necessary permission to run the pipeline through the various territories and ownerships that were involved. That is always a problem whenever pipeline propositions in this country have to be considered. Here, one realizes the necessity of negotiating wayleaves subject to the ordinary cut and thrust of commercial practice. Clearly on the answer to these two questions depends the answer one will get about the economics of the line. It would be interesting to know whether comparisons have been made and it has, in fact, been demonstrated that the transfer cost of materials from Le Havre to the Paris region compares favourably with the cost that would be incurred in using the more conventional methods, *e.g.* water, rail, or road.

It has seemed to me, in following the author's exposition, that the actual planning of the movement of materials from terminal points and ultimately to the depots must be most precisely worked out, the reference on p. 7 that "the monthly statement is further broken down to a more precise weekly statement established by 'planning' in agreement with customers several days before the commencement of each week. This weekly schedule is compulsory and has to be accepted by the companies, who may not ask for any further modifications" is well understood. This seems to be perfectly fair; in fact, it could hardly be conceived how those people who are concerned with what must be a very complicated business could be expected to ask for less if they are to perform their duties properly. On p. 8, however, the author states: "It goes without saying that last-minute changes are frequent as a result of operational incidents at refineries dispatching products and unforeseen modifications requested by receiving depots." Sir Roger de Coverley would have said "there is much to be said on both sides," but that hardly disguises the fact that the statements are contradictory. One can understand the very great difficulties with which the operators are going to be faced unless they have a precise

programme, and one can also understand the complications which the distributors suffer when faced with difficulties at the refinery end from the non-arrival of cargoes, modifications of production schedules, and the like. It would be very interesting to hear more about how these conflicting interests are reconciled in practice.

J. B. Capdeville: Concerning the question of the intervention of the French Government in the joint economy company, it is necessary to say that a certain compromise was obtained between the different interests. The company is under the control of two employees of the Government, one from the Industry and Trade Ministry and the other from the Public Works and Transportation Ministry. These two employees have the right to veto only in a case when the decision of the Board of Directors would be contrary to the general policy of the French Government in matters of oil or transportation. In fact, these Government employees never veto and, if they had to do so, it would be only for a very important question. In the day-to-day operation, the company tries to have the same policy as an ordinary commercial company.

It is thought that the compromise can be continued and that is the reason why we have excellent relations with our customers. I think personally that the French Government has no intention of interfering with the ordinary and day-to-day operation.

There is a very particular situation relating to the right of expropriation. The French Government has the right of expropriation, in the case of a work of public utility, but only the right of expropriation of the soil. For pipelines, the French Parliament promulgated a special law, giving our company only the right of expropriating the subsoil. In fact, after the work of burying the pipeline has been done, the owner of the soil has the right to cultivate his field.

Referring to the economics of the pipeline and the comparison of the cost of different kinds of transportation, the Le Havre–Paris pipeline is in competition with railways and barges. For the railways, there is no comparison, because the rate of the pipeline is half the cost of rail transport.

For a comparison with barges, the problem is more complex. There are special conditions for both water and pipeline transportation between Le Havre and Paris.

The navigation of the Seine cannot be compared with that on the Thames or Mississippi. For instance, the distance between Le Havre and Paris is approximately twice the length of the straight line which the pipeline can follow.

On the other hand, the Le Havre–Paris pipeline is more complicated than pipelines ordinarily are.

It is, in a manner, a distribution pipeline, supplying petroleum products to all the tank farms of the Paris area. For this purpose, it was laid across the suburbs of Paris, where the expense was three times the cost of laying the pipe in the country.

There is also the problem of the load factor for each type of transport. In Paris the consumption of petroleum products in summer is only 65 per cent of winter consumption, when the efficiency of barges is smaller. This situation is causing a considerable lack of balance in the load factor of the barges and the pipeline, more prejudicial for the barges than for the pipeline itself.

In fact, and all elements being taken into consideration, the rate of transportation by pipeline is approximately 20 per cent less than the rate of barges.

However, oil companies which possess their own barges can obtain for them a better load factor and consequently a cost which is approximately the same as the pipeline's rate.

The observation on the planning of the schedule is very pertinent. The weekly schedule is theoretically a compulsory schedule which cannot be changed. In practice, however, it is necessary to take into consideration the conditions at the refineries as well as the tank farms, and to adjust our weekly schedule in relation to the unforeseen difficulties of our customers. We try to operate in that matter with the maximum of flexibility.

There is absolutely no obligation for our customers to transport their products through the pipeline. For the day-to-day operation, we have the policy of a commercial company, and our incentive action is based only on our good rates and the perfect service given to customers.

E. J. Sturgess: Generally speaking, experience shows that it may take up to one year to get pipelines to that state of cleanliness where measurement by meter is satisfactory. Could the author give some information as to how often scrapers had to be passed through the line before it was sufficiently clean for this purpose?

Could he also say how many days operation a year one should count on when working out the maximum capacity of a products pipeline?

J. B. Capdeville: When the pipeline was put into operation, the inside was covered with rust scales produced during the manufacture in the mills. For one year a large quantity of rust in the hay tanks was collected and it was only after that period that the meters could be put in operation. During that time the products were measured by simple gauging in the tanks. The meters were put in operation only after an extensive programme of scrapers. At the very beginning, approximately one scraper per week was put into the line; now it is only one per month. The "C" factor of the Hazen and Williams formula was increased from 135 at the beginning to 155 at present.

This programme of scrapers is completed by injection of inhibitors. Sodium nitrite, or some other organic chemical product, is used, but it is thought that sodium nitrite is sufficient.

For the definition of the maximum capacity of the pipeline, it is considered that a pipeline can run 24 hours per day during a period of six months, for instance. A programme of preventive maintenance can reduce, and even cut out, the breakdowns. Even by taking into account the possible difficulties in the refining process, it is possible to run the pipeline 650 hours per month.

The repairs on the pipeline itself need only a very short time. Replacing a section requires only a 24-hour shutdown.

A. J. Rauscher: I would just like to confirm that the companies are absolutely free to use the pipeline or not and to confirm that they are absolutely satisfied with the way it works.

H. G. B. Nolan: On the question of interfaces, it is believed that this pipeline is about 200 kilometres long; one would anticipate an interface of about 40 cubic metres at the end of the line. Is that the author's experience, or does he find it is sometimes that figure, but much worse at other times? When the pipeline is shut down with the interfaces in the line, is it found that this affects the length of the interface appreciably? Does it lengthen even when the line is shut down under pressure? Are there difficulties in keeping the line shut down under pressure with an interface in it?

The author mentioned that the line had been stopped, due to road repairs or, perhaps, building operations. Have Stopples been used? It is an American invention for cutting into a line under pressure, and putting a loop line round it while the middle section of line is replaced.

On the question of detection of interface, it is gathered that this is done solely by sampling, although the author mentioned that colour can be used. Has colour actually been used and what is the author's experience? Is it possible, with colour, to decide the critical point of cut during the passage of an interface, or does one merely

decide that the moment the colour appears, a cut is made one way, and the moment colour ends the cut is made the other way? In other words, where the interface may last 5 minutes at the end of your line, is it possible to decide the point at the interface at which you cut from one product to another product?

In operating the pipeline through various local authorities in France, do local rates have to be paid on the valuation of the pipeline, as we do in this country?

To revert to operational matters, is the company compelled by law to patrol the pipeline at certain minimum time intervals by foot patrol to see if there are any leaks, or to check that there is no building over the line? Has the company the right to patrol the line at any time it likes, by day or by night, along the actual route of the line, even if it goes through somebody's garden or across a field of standing corn?

Are the pump stations and all depots linked by teleprinter service, so that the quantities of input and output of each batch are recorded on the teleprinter in writing, and not given verbally by telephone?

Finally, on the question of meter preventive maintenance, how many thousands of cubic metres of throughput are allowed between preventive maintenance overhauls?

J. B. Capdeville: It seems that the length of contamination is not only a question of pipeline length. There is a very complicated piping system in the pump stations and terminals, which results in an extension of the contamination and is the reason why the figure of 40 cubic metres cannot be reached. Tests have been made, without decisive result, for studying the shutdown under pressure of the line, with an interface in it. In practice, there is a contamination of about 50 to 100 cubic metres.

The Stopple device developed by Williamson in the U.S.A. is known. Stopples were used during the summer for adjusting piping and valves intended for a new intermediate station. It was verified that the device was completely tight, and it was perfectly possible to cut the line without emptying it. There is only one disadvantage: each device can be applied only for two diameters of pipe, 10-inch and 8-inch.

The colouring of products is very useful in the company's operations, especially for determining the interface between two products of different colour, *e.g.* high-grade benzine coming from two different refineries. The operator at the terminal who has to close the valves in connexion with the arrival of the interface is helped by an assistant who controls the colour of the arriving product with a colour scale prepared in advance according to the percentage of the two colours in the contamination. When it is necessary to determine the interface between two non-coloured products, colour can be injected at the interface in the refinery and the same procedure is used. In each case, the product is taken out of the line by means of a sampling device.

The system of taxes is not the same in England as it is in France. For the pipeline France has the same taxes as the other methods of transportation. Fees have also to be paid for the sections of pipeline occupying ground owned by the French Government, *e.g.* when it crosses a highway or is situated in a harbour. The total of these fees is low, however.

Since 1 October 1956, a new law has been issued by the French Government relating to taxes paid by the conventional ways of transportation, the taxes for pipelines not being modified. However, roughly speaking, it can be said that the comparative tax-rate position is the same for trucks, barges, or pipelines.

The line is patrolled by plane once a week, and all the special points, valves, river crossings, and pipes in crowded areas, are watched once a day. In fact, since the beginning of operations, there have been no leaks and no trouble.

There is a private telephone and telegraph line from the dispatching office to each station and terminal, but there is no teleprinting for meter indication.

There is a printing device on the meters, and many copies are printed of the ticket indicating the volume passed through the meters, including one for the customs administration and one for the customer. This device appears to be sufficient, as teleprinting is an expensive installation.

There are meters through which approximately 200,000 cubic metres have passed without any repair. As a preventive maintenance measure, however, the meters are replaced after a volume of 100,000 cubic metres, because they are, in some ways, the basis of the products accounting system.

B. H. Gibbs: It would be interesting to know if, on the single-faced Flexibox mechanical seals used on the pumps, it was found to be an advantage to start off with these mechanical seals or start off with packing in the pumps. The author mentioned a period of six months which the pipeline took to clean or to descale. There are differences of opinion on this subject, and some engineers consider that packing is best for the start, followed by a change-over to mechanical seals in a fairly short time, at the first overhaul.

J. B. Capdeville: There was some trouble at the very beginning with the mechanical seals, but it was only a question of training personnel. The repair of mechanical seals is more difficult than the repair of ordinary stuffing boxes, but when the repair is perfectly made, the pumps can run for many months without attention. Two kinds of pump were chosen.

A certain number of these pumps was equipped with stuffing boxes and the others with mechanical seals, in order that the comparison could be made. Serious trouble resulted from defective adjustment of the stuffing boxes. It is considered that stuffing boxes require precise manual skill, mechanical seals, on the other hand, demanding only good mechanical knowledge.

Lord Geddes: Each question has shown an extraordinary interest in the paper which Mr Capdeville has given to us, and each of his answers has maintained that high level of interest.

The meeting then closed with a unanimous vote of thanks to the author.

THE DETERMINATION OF MONO- AND DI-AROMATICS IN MINERAL OIL FRACTIONS *

By H. GEELEN †, H. I. WATERMAN † (Hon. Fellow), and J. B. WESTERDIJK †

SUMMARY

A method of calculating the average number of mono-aromatic rings R_A^{I}, di-aromatic rings R_A^{II}, and naphthenic rings R_N in oil fractions is described.

Use is made of the diagrams of the specific refraction, the specific volume ($1/d$), and percentage hydrogen as functions of the reciprocal of the molecular weight and of the molecular weight of saturated fractions. If these diagrams are applied to aromatic fractions an apparent ring number is found. There exists a linear relation between these apparent ring numbers and R_N, R_A^{I}, and R_A^{II}. With the three diagrams three relations are found from which R_A^{I}, R_A^{II}, and R_N are solved. Formulæ are given from which these ring numbers can be calculated directly from specific refraction, specific volume, and molecular weight. The relations are checked by analytical hydrogenation of the fractions (values taken from the literature). The influence of tri-aromatics on these calculations is studied and is found to be small.

The method is applied to type concentrates prepared by chromatographic methods. It is found that by the analytical hydrogenation of oil fractions the di-aromatics are first hydrogenated to mono-aromatics and then the mono-aromatics to saturated products.

INTRODUCTION

For mineral oil fractions with an average molecular weight of 150 to about 500, different methods are available for the determination of their structural analysis making use of physical constants. These methods enable us to determine the average number of aromatic rings per molecule and the percentage of carbon present in aromatic structure.[1,2] These methods can be used only if the number of aromatic rings is not too high.

If the methods are applied to fractions with a high degree of aromaticity or to fractions which differ strongly from those obtained by distillation of crude mineral oils, then deviations are observed. These deviations are caused by the different types of aromatics, which are present in varying proportions. Molecules with a benzene nucleus (mono-aromatics) have physical constants quite different from molecules with a naphthalene nucleus (di-aromatics). Mono-aromatics are molecules with one or more benzene nuclei which are not fused, such as alkylbenzene and tetralin derivatives. In the case of saturated ring systems, however, it does not make much difference if two isolated *cyclo*hexane rings or if a decalin ring system is present in the molecule. The influences of mono- and di-aromatics on the physical constants have to be studied separately.

Di-aromatics are molecules with one or more naphthalene nuclei which are fused neither mutually nor with a benzene nucleus. Alkylnaphthalenes, therefore, are di-aromatics. The average number of mono-aromatic rings per molecule is indicated by R_A^{I} and the average number of di-aromatic rings by R_A^{II}. For an alkylnaphthalene R_A^{II} is equal to two.

The influence of the mono- and di-aromatics on the various specific functions used in the analysis will be studied below.

SPECIFIC FUNCTIONS FOR SATURATED HYDROCARBONS AND HOMOLOGOUS SERIES OF HYDROCARBONS

For saturated fractions there exists a simple relation between a specific function, the molecular weight M and the average number of rings per molecule.

In this investigation the specific refraction $r_{\mathrm{spec}} = \dfrac{n^2-1}{n^2+2}\cdot\dfrac{1}{d}$ (Lorentz–Lorenz) and the specific volume $\dfrac{1}{d}$ were studied, where n denotes the refractive index and d the density. The considered relations are represented by the well-known figures of the " fan " type (cf Figs 1 and 2).

The basis of these diagrams is formulæ which have been derived from the measured physical constants of a large number of saturated mineral oil fractions from different sources.

The average number of rings R of these fractions had been determined before by means of the results obtained by the n–d–M method.[1] The formulæ are :

$$r_{\mathrm{spec}} = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d} = 0{\cdot}3310 + \frac{1{\cdot}419 - 1{\cdot}654R}{M} \qquad (1)$$

$$\frac{1}{d} = 1{\cdot}1749 + \frac{27{\cdot}56 - 16{\cdot}32R}{M} \qquad (2)$$

If the formulæ (1) or (2) or the diagrams (Figs 1 or 2) are applied to pure hydrocarbons or to mineral

* MS received 12 September 1956.

† University of Chemical Engineering, Delft, Holland.

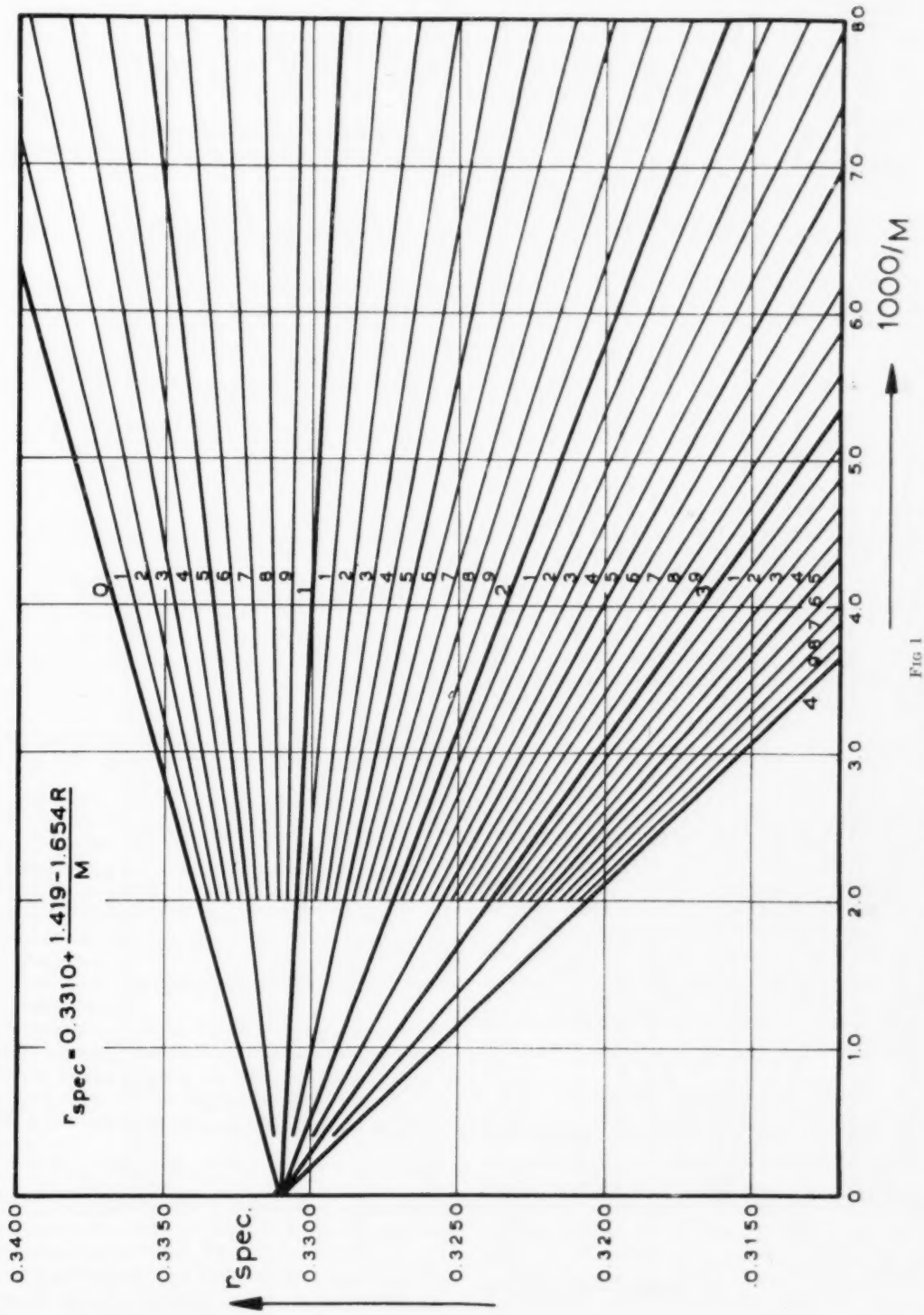

FIG 1

RELATION BETWEEN SPECIFIC REFRACTION, MOLECULAR WEIGHT, AND NUMBER OF RINGS

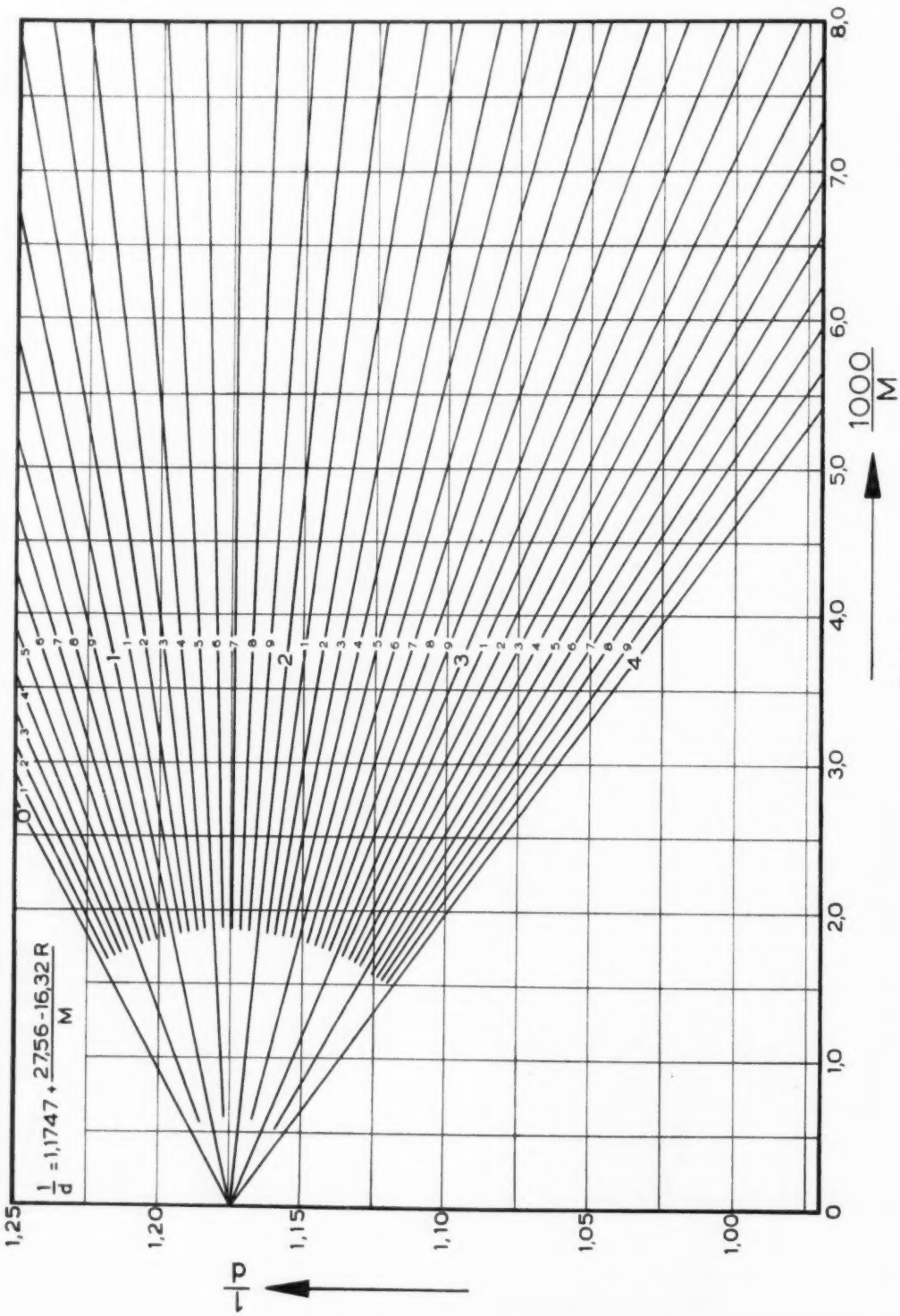

FIG 2

RELATION BETWEEN SPECIFIC VOLUME, MOLECULAR WEIGHT, AND NUMBER OF RINGS

oil fractions containing aromatics, an apparent number of rings is found. This apparent number depends on the structure of the hydrocarbon(s). Only for saturated (aromatic-free) mineral oil fractions does it equal the real average number of rings per molecule.

For the members of a homologous series of hydrocarbons the same apparent number of rings is always found. Therefore the series can be characterized by an apparent number of rings.

In Table I these apparent numbers of rings are given for some series of homologous hydrocarbons.

TABLE I

Average Apparent Number of Rings per molecule for some Homologous Series

	From specific refraction R_r	From specific volume R_d
n-Alkanes	0·02	0
n-Alkyl*cyclo*hexanes	0·94	1·04
1-*n*-Alkyldecalins	1·99	2·15
2-*n*-Alkyldecalins	1·97	2·16
n-Alkylbenzenes	0·46	1·77
1-*n*-Alkyltetralins	1·38	2·87
1,1-Diphenyl *n*-alkanes	0·93	3·55
1-*n*-Alkylnaphthalenes	−0·34	3·37
2-*n*-Alkylnaphthalenes	−0·57	3·23

The physical constants which were used for the calculation are taken from the tables of API Research Project 44.[3]

APPARENT NUMBER OF RINGS IN MINERAL OIL FRACTIONS CONTAINING AROMATICS

For mineral oil fractions the apparent ring number depends on the average number of naphthenic rings per molecule R_N, the average number of mono-aromatic rings R_A^{I}, and the average number of di-aromatic rings R_A^{II}. In mineral oil fractions the average branching of the molecules does not vary very much, therefore the influence of branching can be neglected. Aromatics with more than two condensed benzene rings are provisionally left out of consideration.

The mixing rule, with which the specific functions of a mixture can be calculated from the specific values of the components and their percentages of weight, can also be applied to the ring numbers. Then the apparent ring number can be calculated from

$$R_r = R_N + xR_A^{\mathrm{I}} + yR_A^{\mathrm{II}} \quad . \quad . \quad (3)$$

In formula (3) x denotes the apparent ring number for a hydrocarbon with only one aromatic ring and y the apparent ring number for a hydrocarbon with only one di-aromatic ring. The constants x and y for the various specific functions can be calculated from pure hydrocarbons. Using the values given in Table I, one finds

$$R_r = R_N + 0{\cdot}46R_A^{\mathrm{I}} - 0{\cdot}23R_A^{\mathrm{II}} \quad . \quad (4)$$

The factor −0·23 for the di-aromatic rings has been obtained by taking the average value of the 1- and 2-*n*-alkylnaphthalenes: $\frac{-0{\cdot}34 - 0{\cdot}57}{2} = -0{\cdot}46$, which is −0·23 per single di-aromatic ring. No aromatics higher than di-aromatics are taken into consideration.

The influence of mono- and di-aromatic rings on the specific refraction proves to be completely different. In an earlier paper [4] it has been stated that for mineral oil fractions containing aromatics the specific refraction diagram (Fig 1) gives us an average number of rings R_r equal to the number of naphthenic rings R_N.

Regarding the small factors for R_A^{I} and R_A^{II} and also the fact that they are positive and negative, respectively, it can be expected that R_r equals R_N as indicated above, if there are approximately equal amounts of mono- and of di-aromatics present.

If one applies the same considerations to the specific volume, it can be found from Table I that the apparent ring number obtained by applying formula (2) or Fig 2 is given by

$$R_d = R_N + 1{\cdot}77R_A^{\mathrm{I}} + 1{\cdot}65R_A^{\mathrm{II}} \quad . \quad (5)$$

In this case the factor for the di-aromatics has also been calculated from the average value of the 1- and 2-*n*-alkylnaphthalenes, whilst the presence of higher aromatics is neglected. It seems that for the specific volume there is only a small difference between the mono- and the di-aromatic rings. The two specific functions discussed above form the basis of the *n–d–M* method.[1]

It has now been elucidated why no difference had to be made between mono-aromatic and di-aromatic rings in the application of this method. In the diagram for the specific refraction, mono- and di-aromatic rings compensate each other's influence, so that only the influence of naphthenic rings remains. In the diagram for the specific volume, mono- and di-aromatic rings have about equal influence.

The difference between the ring numbers according to the specific refraction and the specific volume is therefore a measure of the total number of aromatic rings.

This can also be interpreted as follows. If the specific volume (or the density) of saturated (aromatic-free) mineral oil fractions is drawn in the specific refraction diagram, then for mineral oil fractions containing aromatics the difference between the read and the experimentally determined specific volume (or the density) can be calculated by means of the diagram. This difference is a measure of the total number of aromatic rings. This is the principle of the so-called Leendertse density method.[1]

THE CALCULATION OF THE AVERAGE NUMBER OF MONO- AND DI-AROMATIC RINGS IN MINERAL OIL FRACTIONS

Two formulæ were derived in the preceding paragraphs which are used to calculate the three numbers R_A^{I}, R_A^{II}, and R_N. For this calculation a third equation is needed which can be derived with the aid of the percentage of hydrogen. If the mineral oil fraction in question does not contain hetero compounds, the equation can be exactly derived. For saturated (aromatic-free) mineral oil fractions the average numbers of rings can be calculated from the percentage of hydrogen (H) and the molecular weight.

$$H = 14{\cdot}37 + \frac{172{\cdot}6 - 172{\cdot}6R}{M} \quad . \quad . \quad (6)$$

It can be theoretically shown that the apparent ring number R_H, which is found if equation (6) is applied to fractions containing aromatics, is represented by the equation

$$R_H = R_N + 4R_A^{\mathrm{I}} + 3{\cdot}5R_A^{\mathrm{II}} \quad . \quad . \quad (7)$$

In this case also no aromatics higher than di-aromatics are taken into consideration.

If the fraction does contain elements other than carbon and hydrogen, the equation (7) does not hold. The specific refraction and the specific volume are also dependent on the hetero atoms present.

From the three equations (4), (5), and (7), R_N, R_A^{I}, and R_A^{II} can be solved; it is shown later which corrections have to be made for the presence of hetero atoms.

The derived equations are:

$$R_A^{\mathrm{I}} = 1{\cdot}046R_r - 2{\cdot}109R_d + 1{\cdot}063R_H \quad . \quad . \quad (8)$$

$$R_A^{\mathrm{II}} = -1{\cdot}261R_r + 2{\cdot}001R_d - 0{\cdot}741R_H \quad . \quad (9)$$

$$R_N = 0{\cdot}229R_r + 1{\cdot}430R_d - 0{\cdot}659R_H \quad . \quad . \quad (10)$$

It is not necessary to determine first the apparent ring numbers. The equations of the apparent ring numbers (4), (5), and (7) can be connected with the equations (1), (2), and (6) and then R_N, R_A^{I}, and R_A^{II} can be solved. It is convenient to make use of the following additional notations:

$$\Delta r = 0{\cdot}3310 - r_{\mathrm{spec}}$$

$$\Delta\frac{1}{d} = 1{\cdot}1747 - \frac{1}{d}$$

$$\Delta H = 14{\cdot}37 - H$$

Equations (8), (9), and (10) then become:

$$R_A^{\mathrm{I}} = -1{\cdot}60 + (0{\cdot}632\Delta r - 0{\cdot}129\Delta\frac{1}{d} + 0{\cdot}00616\Delta H)M \quad . \quad (11)$$

$$R_A^{\mathrm{II}} = 1{\cdot}56 - (0{\cdot}762\Delta r - 0{\cdot}123\Delta\frac{1}{d} + 0{\cdot}00429\Delta H)M \quad . \quad (12)$$

$$R_N = 1{\cdot}95 + (0{\cdot}138\Delta r + 0{\cdot}0876\Delta\frac{1}{d} - 0{\cdot}00382\Delta H)M \quad . \quad (13)$$

If the fractions contain sulphur a correction has to be made. So far as is known up to now only R_N has to be corrected. The correction is $\Delta R = -0{\cdot}001MS$, where S denotes the percentage of sulphur in the investigated mineral oil fraction and M the average molecular weight.

In Table II a summary of the calculation is given. Table III shows an example.

TABLE II

Calculation of the Average Number of Naphthenic Rings R_N, mono-Aromatic Rings R_A^{I}, and di-Aromatic Rings R_A^{II} per Molecule

(1) Determine:

Refractive index $n_{\mathrm{D}}^{20} = n$, percentage of hydrogen H, density $d_4^{20} = d$, percentage of sulphur S, molecular weight M.

(2) Calculate:

Specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d} = r_{\mathrm{spec}}$, specific volume $\frac{1}{d}$,

$\Delta r = 0{\cdot}3310 - r_{\mathrm{spec}}$, $\Delta\frac{1}{d} = 1{\cdot}1747 - \frac{1}{d}$, $\Delta H = 14{\cdot}37 - H$.

Calculate:

$$R_A^{\mathrm{I}} = -1{\cdot}60 + (0{\cdot}632\Delta r - 0{\cdot}129\Delta\frac{1}{d} + 0{\cdot}00616\Delta H)M$$

$$R_A^{\mathrm{II}} = 1{\cdot}56 - (0{\cdot}762\Delta r - 0{\cdot}123\Delta\frac{1}{d} + 0{\cdot}00429\Delta H)M$$

$$R_N = 1{\cdot}95 + (0{\cdot}138\Delta r + 0{\cdot}0876\Delta\frac{1}{d} - 0{\cdot}00382\Delta H - 0{\cdot}001S)M$$

TABLE III

Example of the Calculation of R_A^{I}, R_A^{II}, and R_N (cf Table II)

Venezuelan residue, fraction 4^1.

(1) $n_{\mathrm{D}}^{20} = 1{\cdot}5144$, $d_4^{20} = 0{\cdot}9229$, % $H = 11{\cdot}87$, % $S = 1{\cdot}93$, $M = 309$.

(2) $r_{\mathrm{spec}} = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d} = 0{\cdot}3264$, $\frac{1}{d} = 1{\cdot}0835$, $\Delta r = 0{\cdot}0046$, $\Delta\frac{1}{d} = 0{\cdot}0912$, $\Delta H = 2{\cdot}50$.

(3) $R_A^{\mathrm{I}} = 0{\cdot}42$, $R_A^{\mathrm{II}} = 0{\cdot}63$, $R_N = 1{\cdot}07$.

Check (see below)

Direct method	$R_T = 2{\cdot}13$	$C_A = 5{\cdot}5$
calculation	$R_T = 2{\cdot}12$	$C_A = 5{\cdot}7$
n-d-M method	$R_T = 2{\cdot}17$	$R_A = 0{\cdot}90$

CHECK ON THE EQUATIONS FOR R_N, R_A^{I}, AND R_A^{II}

A check on the results can be obtained by analytical hydrogenation of the fraction.

From the ultimate analysis and the molecular weight of the fraction before and after hydrogenation the average number of aromatic carbon atoms per molecule C_A can be calculated.

The average number of aromatic rings per molecule

cannot be derived from the average number of carbon atoms in the aromatic structure. It is necessary to know the amount of mono- and di-aromatics or a certain assumption as to the nature of the ring structure has to be made. A mono-aromatic ring contains six aromatic carbon atoms, whilst a di-aromatic ring contains five such atoms

$$C_A = 6R_A^{\mathrm{I}} + 5R_A^{\mathrm{II}} \quad . \quad . \quad . \quad (14)$$

From the formulæ for the calculation of percentage C_A and the total number of carbon atoms per molecule [1] it follows that

$$100C_A = 0{\cdot}9921(M^1H^1 - MH) - 0{\cdot}1655\,(M^1C^1 - MC) \quad . \quad (15)$$

There M^1, H^1, and C^1 denote the molecular weight, percentage of hydrogen, and percentage of carbon of the hydrogenated fraction; M, H, and C represent the same values of the original fraction before hydrogenation. The total number of rings can be calculated by means of equation (6), applied to the hydrogenated fraction.

From a number of fractions discussed in the literature the calculation of R_N, R_A^{I}, and R_A^{II} can be made and the results compared with the check method described above. The results are combined in Table IV.

TABLE IV

Check on the Calculation of mono- and di-Aromatics by Analytical Hydrogenation

Literature	Number of fractions	Average deviation	
		C_A	R_T
van Nes and van Westen [1] .	29	0·3	0·08
Martin and Sankin [5] * . .	20	0·6	0·14
Mair, Willingham, and Streiff [6]	4	0·2	0·14

* For a certain number of fractions $\%\ S$ was not determined; an approximation can be obtained by assuming $\%\ S$ to be equal to half of the percentage of weight of the hetero atoms.

The average deviation from C_A seems to be about 0·4, which is equivalent to about 0·1 ring, the deviation of R_T being 0·1 ring.

For a certain number of fractions a negative value of R_A^{I} was found. These are generally fractions in which the presence of tri-aromatics (phenanthrene and/or anthracene derivatives) is possible. From a study of phenanthrene derivatives (anthracenes are practically absent in mineral oil fractions) it seems that in the presence of higher aromatics the total number of rings, R_T, which is calculated with the method described in this paper ($R_T = R_N + R_A^{\mathrm{I}} + R_A^{\mathrm{II}}$), is somewhat too high.

The calculated values for R_A^{I} and R_A^{II} deviate considerably. The calculated total number of aromatic rings ($R_A^{\mathrm{I}} + R_A^{\mathrm{II}}$) seems to be in good agreement with the real number of aromatic rings. The presence of phenanthrenes lowers the calculated R_A^{I}, but increases the value which is calculated for R_A^{II}.

Therefore, in the presence of tri-aromatics, the method can be applied only to the calculation of the total number of aromatic rings per molecule.

SOME APPLICATIONS OF THE METHOD

(1) *Hydrogenation of Fractions Containing Aromatics*

In the book by van Nes and van Westen [1] a large number of fractions, obtained as intermediate products in the analytical hydrogenation, is described.

Of these products the ultimate analysis has been made and the physical constants determined. With the aid of these determinations the average number of mono- and di-aromatic rings can be calculated. If one represents graphically the course of the hydrogenation and, in particular, the mono- and di-aromatic rings, it is observed that the number of mono-aromatic rings initially increases and afterwards decreases, whilst first the di-aromatics are transformed into mono-aromatics and later the mono-aromatics are hydrogenated (*cf* Fig 3).

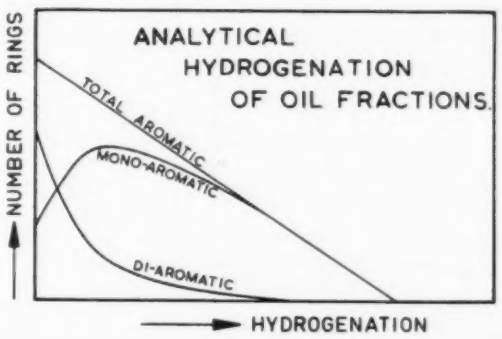

FIG 3

In this connexion it must be remarked that the method is not very suitable for almost-saturated fractions, for which the number of rings is determined better by other means.

(2) *Application to Type Concentrates*

The method was applied to three type concentrates which had been obtained by a chromatographic separation from a so-called "Kerex," namely, a saturated, a mono-aromatic, and a di-aromatic fraction. These concentrates were kindly placed at our disposal by the Royal Dutch/Shell Laboratories, Amsterdam.

The physical constants and the ultimate analysis of these fractions are given in Table V. In this

table the results of the mono- and di-aromatics and of the *n–d–M* method are also mentioned.

TABLE V

Type Concentrates ex "Kerex"

	Saturated concentrate	Saturated concentrate after oxygen removal	Mono-aromatic concentrate	Di-aromatic concentrate
n_D^{20}	1·4560	1·4546	1·5071	1·5958
d_4^{20}	0·8229	0·8213	0·8982	0·9940
M	197	206	181	167
$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	0·3303	0·3301	0·3314	0·3423
$\frac{1}{d}$	1·2152	1·2176	1·1133	1·0060
% H	13·63	14·04	10·95	7·83
% C	86·01	85·90	88·73	91·91
% S	0·01	—	0·03	0·11
100 − (% H + % C + % S)	0·35	0·06	0·29	0·15
R_A^{I}	0·41	0·08	0·73	0·30
R_A^{II}	−0·15	0·04	0·33	1·78
P_N	0·88	0·94	0·55	−0·01
R_T	1·14	1·06	1·61	2·07
R_T (*n–d–M* method)	1·08	1·07	1·64	1·55
R_A (*n–d–M* method)	0·13	0·09	0·77	1·91

The ultimate analysis proved that the saturated-type concentrate still contains 0·35% of hetero atoms, probably oxygen. The oxygen compounds are removed by treating this concentrate in a column of Al_2O_3, washing with pentane. After separation from the pentane the concentrate was again analysed; the results obtained are also given in Table V. It was almost oxygen-free.

Comparison of the results of the mono- and di-aromatics analysis with the results of the *n–d–M* method shows that for the saturated fractions the results are in reasonable agreement. For the mono-aromatic fraction the total number of rings according to both methods is almost equal; the total number of aromatic rings differs considerably.

Probably the value of R_A determined by the *n–d–M* method is too low. In the case of the di-aromatic fraction the results of each method are quite different. The results of the *n–d–M* method are not reliable in this case; the results of the mono- and di-aromatics analysis are satisfactory.

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MODULUS OF RIGIDITY AND PENETRATION OF PARAFFIN WAXES *

By W. M. MAZEE †

SUMMARY

The mechanical properties of paraffin wax are important in regard to its behaviour in practice. As the penetration is not a good criterion for the rheological behaviour of waxes, other magnitudes had to be measured. It was found that the modulus of rigidity of paraffin wax gives valuable information on the mechanical properties of the material. A simple apparatus for determining the modulus of rigidity is described.

The procedure consists in measuring the deformation in a bar of the wax on submitting it to a shearing stress at various temperatures.

The modulus of rigidity is more sensitive to temperature than is penetration and gives a far better differentiation between waxes of the same type but of various origins.

INTRODUCTION

Among the mechanical properties of petroleum waxes their "hardness" occupies an important position. "Hardness," without being defined more closely, is generally assumed to be characterized by the result of the penetration test. Whether the penetration figure is actually a satisfactory measure of this quality is very much open to doubt. Several years ago Minchin [1] stated, "It has not found acceptance for testing commercial grades of paraffin, probably because it gives variable results with these products." This author therefore developed two other tests for measuring hardness: a "cone hardness" test, in which, under given conditions, a cone penetrates into the wax, and a "ball hardness" test, in which the depth of the impression made by a ball is measured. The results of these two methods also show differences, ascribed by Minchin to "the fact that the ball test is somewhat more compressive, and the cone test somewhat more shearing, in nature." This statement, in fact, clearly shows the difficulties attaching to these tests: we do not know the quantitative contributions of shear and compression.

With this fact in mind, a new method has been developed at the Koninklijke/Shell-Laboratorium, Amsterdam. It is a simple technique for measuring the modulus of rigidity of wax and it is believed to give information only on the resistance to shear.

APPARATUS FOR MEASURING THE MODULUS OF RIGIDITY OF WAX

(1) *Principle of the Method*

A rectangular bar of paraffin wax is held by its two ends in clamps A and B (Fig 1).

Clamp A is fixed and clamp B can be subjected by means of a weight to a force at right angles to the longitudinal axis of the bar. After some time the upper surface of the wax specimen will have moved over a distance Δl. If this displacement is propagated uniformly throughout the bar it will be deformed in such a way that its right angles change by an amount γ. The angle γ is called the angle of shear. According to Hooke's law we may, to a first approximation, expect proportionality between the shearing stress exerted (if this is low) and the resultant

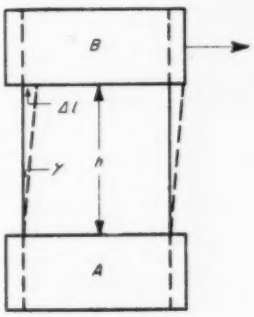

Fig 1

DIAGRAM OF SHEAR SYSTEM IN THE DETERMINATION OF THE MODULUS OF RIGIDITY

deformation. The angle will then be determined by the shearing force (τ) per unit area. Thus

$$G = \frac{\tau}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where G is the modulus of rigidity, a shearing stress characteristic of the material.

(2) *Apparatus and Procedure*

The molten wax is poured into a rectangular mould. After cooling, the bar thus formed is cut into specimens measuring about $40 \times 20 \times 10$ mm. Together with the apparatus (Fig 2) these are placed in a stove maintained at the required temperature. After at least 2 hours one of the specimens is carefully placed in clamps A and B. By tightening screws I, plates K, which are saw-toothed on the side facing the specimen, are pressed against it. The bar cannot slip in the clamps, as the teeth point downwards. The load exerted by a weight G is transmitted via

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pulley H to clamp B, which can move along the guide rail. The vernier C moves along a scale on rail R. As a rule readings of the displacement are taken at the end of 15, 30, 45, and 60 minutes. They are accurate to within 0·05 mm. The modulus of rigidity is calculated only from the angle of displacement at the end of 60 minutes and for small angles can be derived from $\gamma = \frac{\Delta l}{h}$, where h is the vertical distance between the clamps. The other observations only serve to examine the progress of shear, which may be irregular, for instance if cracks have developed in the bar.

It was found that the reproducibility of the measurements of the modulus of rigidity was about ± 5 per cent. This figure remains constant for the whole range of temperatures at which measurements were carried out.

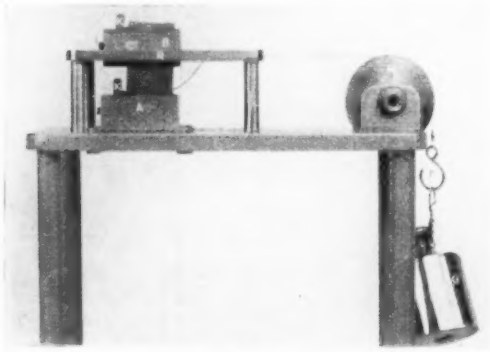

FIG 2

APPARATUS FOR THE DETERMINATION OF THE MODULUS OF RIGIDITY

INFLUENCE OF SHEARING STRESS ON MODULUS OF RIGIDITY

As will be seen from some examples in Table I, the modulus of rigidity drops slightly with increasing shearing stress.

TABLE I

Wax grade	Temp., ° C	τ = $5{\cdot}5 \times 10^4$ dynes/cm² G in 10^5 dynes/cm²	τ = $1{\cdot}1 \times 10^5$ dynes/cm² G in 10^5 dynes/cm²	τ = $2{\cdot}2 \times 10^5$ dynes/cm² G in 10^5 dynes/cm²	τ = $5{\cdot}5 \times 10^5$ dynes/cm² G in 10^5 dynes/cm²
Wax A 135/140 .	40	3·9	3·6	2·1	—
Wax B 125/130 .	30	—	14	11	7·8
Wax B 125/130 .	32·5	6·8	6·1	4·5	—
Wax C 138/140 .	40	12	10	—	—

The decrease in the modulus of rigidity is due to several causes. After a given interval of time the angle of shear increases more than in proportion to the stress. Extensive investigations, in which the modulus of rigidity was measured by means of torsion experiments, have brought to light that the deformation of paraffin wax may be thought of as consisting of three parts: purely elastic deformation, retarded elastic deformation, and viscous flow. Since at the highest loads the deformation became fairly large, the influence of viscous flow is relatively great under these conditions. It was found that the viscous flow, in particular, was subject to non-linearity. Consequently, the modulus of rigidity then measured was lower than at smaller deformations.

Numerous measurements of the modulus of rigidity, both by the torsion method and by the "shear method" described above, have demonstrated that its value is constant and the same for the two methods, provided that the value of γ does not exceed about 0·01. In the experiments reported here, γ was of the order of 0·1 to 0·3. It seemed useful to measure the modulus of rigidity at this somewhat greater deformation, because in many problems arising in actual practice viscous flow will play an important role. In comparative measurements on waxes, however, excessive variations in shearing stress should be avoided.

SIGNIFICANCE OF THE MODULUS OF RIGIDITY

When liquid paraffin wax crystallizes the components with the highest melting points form crystals first.[2] Later on in the cooling process the lower-melting waxes will constitute a relatively soft layer between the hard crystals of higher melting point. When the solid wax is deformed this layer acts as a lubricating film and thus plays an important part.

This concept of crystallized wax has been confirmed by measurements of the modulus of elasticity (a property closely related to the modulus of rigidity) and by measurements of the damping of vibrations generated in bars of wax. If one plots damping against the prevailing temperature, curves with a maximum are obtained. The same type of curve was observed by Zener[3] for aluminium, who attributed the maximum to the occurrence of a more or less "amorphous" material at the crystal boundaries. In the case of paraffin wax the corresponding effect will be produced by a softer wax or by extensive disturbances in the lattice at the crystal faces.

At about 10° C below the melting point of a pure hydrocarbon or a narrow fraction of paraffin wax, the modulus of rigidity commences to drop sharply with increasing temperature. In the case of a commercial wax, the sudden drop appears approximately at a temperature corresponding to that observed for the low-melting part of the wax. As this part forms the "lubricating film" between the hard crystals, it thus to a great extent determines the rigidity characteristics of the total wax. Measurements of the deformation of paraffin waxes should be carried out on a relatively large bulk of material, in order that the latter may be considered as homogeneous. In the rigidity test described here this requirement is

fulfilled: the crystal size is very small in relation to the sample. In the penetration and similar tests the above condition is often far from satisfied.

COMPARISON OF MODULUS OF RIGIDITY AND PENETRATION

In order to compare the values of the modulus of rigidity and the penetration, some measurements have been carried out on commercial waxes of widely different origins. The results are recorded in Table II.

TABLE II

Wax grade	Temp ° C	Penetration[a]	G in 10^5 dynes/cm^2	Pen. 40° C / Pen. 35° C	G 35° C / G 40° C	Pen. relative to wax P	G of wax P / G of wax X
Wax D 135/140	25	15	—	—	—	—	—
	35	27	49	2·4	9·1	1·8	2·2
	40	66	5·4			3·1	10
Wax E 135/140	25	13	—	—	—	—	—
	35	30	10	1·8	14·7	2	11
	40	54	0·68			2·6	81
Wax H 135/140	25	12	—	—	—	—	—
	35	21	33	2·0	15·7	1·4	3·3
	40	43	2·1			2·0	26
Wax C 138/140	25	14	—	—	—	—	—
	35	18	52	2·4	5·2	1·2	2·1
	40	43	10			2·0	5·5
Wax P 140/145	25	12	—	—	—	—	—
	35	15	110	1·4	2·0	1	1
	40	21	55			1	1

[a] ASTM D1321-54T (100 g, 5 sec).

The figures call for the following comments. The penetration at 25° C (the temperature at which it is generally determined) shows very little variation. The lowest figure is 12, the highest 15. Now, ASTM D1321–54T mentions a reproducibility of 3 and a repeatability of 2 points at this level. Therefore one can scarcely speak of any difference in penetration at 25° C. At other temperatures, also, the penetration provides little information. At 35° C wax D 135/140 has a modulus of rigidity about five times that of wax E, whilst their penetrations are again about equal (27 and 30 respectively). Similarly, at 40° C waxes H and C have the same penetration (43), whereas the modulus of rigidity of C is about five times that of H. This means that at a given load the deformation of wax H is five times greater than that of C, or, in other words, C is deformed to the same extent as H under a load that is five times as high. Penetration values would never have allowed of this conclusion. Sometimes penetration and modulus of rigidity are in fair agreement, for instance, with the same waxes C and H at 35° C (pen. 21 and 18; G 33 $\times$ 10^5 and 52 $\times$ 10^5 dynes/cm^2).

It further appears that the changes in penetration with the temperature are much less marked than those of the modulus of rigidity (col. 5 and 6 of Table II). The penetration ratios become even more doubtful when the penetration reaches values of about 50 or more. The ASTM method indicates a reproducibility of 8 points at pen. 50 and of 39 points at pen. 150.

The ratios between the penetrations at 40° and 35° C of waxes D and C are both 2·4; their dependence on temperature would therefore seem to be the same, but the ratios between the moduli of rigidity show up a considerable difference (9·1 and 5·2 respectively).

The relative lack of meaning of the penetration is more evident if one compares the waxes. Let us consider what would be called the "hardest" commercial wax, P 140/145. Comparing products C and H with P at 40° C, it is found that in both cases the penetration ratio is 2. One would therefore be inclined to think that wax P is twice as "hard" as both C and H. But the ratios of the ridigity moduli are 26 and 5·5, respectively, figures which allow of a much clearer differentiation. In other words, at this temperature wax P 140/145 is 5·5 times more resistant to deformation than wax C 138/140, and 26 times more so than wax H 135/140 if the same shearing stress is applied.

In accordance with these observations it was, for instance, found that the wilting at certain temperatures of candles made from the various waxes could be predicted from the values of the moduli of rigidity, low values always being paralleled by marked wilting. The penetration did not give any indication whatsoever in this respect.

Another field in which determination of the modulus of rigidity can prove very useful is the modification of the properties of a paraffin wax by the addition of microcrystalline wax or ceresin or of high-melting waxes. It is common knowledge that in the waxed paper and cardboard industry such substances are often added, for instance, to enhance the "strength" of the wax.

The influence of such additions upon penetration and modulus of rigidity is illustrated in Table III.

It is quite clear that the penetration is entirely unaffected by the addition of the second wax and therefore does not reflect the improvement in wax properties. On the other hand, the moduli of rigidity become three to six times as high for the 135/140 grade K, and 2 to 2·3 times as high for M. This implies that under similar conditions these mixtures containing microcrystalline wax are several times more resistant to deformation than are the original grades.

This latter fact is in accordance with what is observed in practice with milk cartons. The "strength" of a wax has to meet certain requirements; below a certain limiting "strength" the cartons often become leaky on transport. The wax is improved by adding a small amount of high-melting wax. This increases its tensile strength, but, what is perhaps even more important, the wax becomes less subject to deformation under equal stresses. Leakage of the milk cartons will therefore occur much less frequently, as is indeed found in actual practice.

TABLE III

Wax grade	Temp, °C	Penetration	Modulus of rigidity, 10^5 dynes/cm²	Pen. sample 2 / Pen. sample 1	G sample 2 / G sample 1	Pen. sample 3 / Pen. sample 1	G sample 3 / G sample 1
Wax K 135/140 (Sample 1)	25	12	—				
	35	19	12	1	3·8	1	6·4
	40	43	3·6	1	3·1	1	3·3
Wax K 135/140 + 1% of microcrystalline wax, cong. pt. 82° C (Sample 2)	25	13	—				
	35	19	46				
	40	42	11				
Wax K 135/140 + 0·75% of synthetic Fischer–Tropsch wax, cong. pt. 102° C (Sample 3)	25	12	—				
	35	19	77				
	40	42	12				
				Pen. sample 5 / Pen. sample 4	G sample 5 / G sample 4		
Wax M 125/130 (Sample 4)	25	14	—				
	32·5	26	6·1	1	2·3		
	35	88	1·8	1	2·0		
Wax M 125/130 + 1% of microcrystalline wax, cong. pt. 82° C (Sample 5)	25	13	—				
	32·5	25	14				
	35	86	3·6				

MODULUS OF RIGIDITY AND PENETRATION OF MICROCRYSTALLINE WAXES

Measurements have furthermore been carried out on several microwaxes as such in order to find out whether for this type of product the determination of the modulus of rigidity also offers advantages over that of the penetration. Table IV gives some results.

TABLE IV

(G = modulus of rigidity in 10^5 dynes/cm²)

Wax grade	Congealing point, °C	25° C		30° C		35° C		40° C		45° C	
		Pen.	G	Pen.	G	Pen.	G	Pen.	G	Pen.	G
R, light yellow	62	21	66	23	42	29	26	39	7·1	88	1·4
S, white	75	18	150	22	—	37	48	65	36	156	18
X, brown	64	44	24	100	8·4	186	5·7	—	2·0	—	—
Y, yellow	68	20	55	25	45	34	18	60	12	119	—
Z, white	61	18	—	21	160	34	53	48	34	108	10

The penetration of waxes S, X, and Y is about equally sensitive to changes in temperature as the modulus of rigidity. With R and Z the modulus of rigidity is much more affected than the penetration. Furthermore, the figures for the modulus of rigidity show more differentiation than those for the penetration. Compare, for instance, wax R, light yellow, and wax Z, white at 30° C. These have virtually the same penetration, but the modulus of rigidity of Z at this temperature is about four times as high as that of R. In the case of the other waxes, again, a far better differentiation is observed in the modulus of rigidity.

Therefore, although the penetration provides more information with microcrystalline than with macrocrystalline wax, it will be evident from the above examples that determination of the modulus of rigidity is undoubtedly preferable.

CONCLUSION

In the first place penetration measurements have the disadvantage of showing a poor reproducibility when applied to paraffin waxes. As waxes, at a given temperature, differ only little in penetration, this poor reproducibility renders differentiation impossible. Moreover, it is not clear what exactly is measured in the penetration test; it is difficult, if not impossible, to describe the physical mechanism.

The modulus of rigidity not only permits of a much better differentiation between waxes, but is also far more dependent on temperature than the penetration.

Furthermore, one can attach a physical significance to the modulus of rigidity and a clear concept can be formed of what happens to the wax in this test.

All these facts, combined with the simplicity of the equipment required for this measurement, render the determination of the modulus of rigidity a very attractive means of characterizing the rheological properties of paraffin waxes.

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	Feed	Product	Feed	Product	Feed	Product
Total C_5-C_6						
Vol. %	100.0	97.3	100.0	96.7	100.0	99.2
Octane CFRR-Clear	63.7	77.7	62.1	77.0	72.3	83.3
+3 cc TEL	88.3	96.2	87.3	95.8	93.9	99.8
Pentane Fraction						
Vol. %	45.0	45.0	34.5	34.5	58.5	58.5
Octane CFRR-Clear	74.4	91.0	72.9	91.0	79.2	91.0
+3 cc TEL	95.8	104.9	94.9	104.9	98.4	104.9
Hexane Fraction						
Vol. %	55.0	52.3	65.5	62.2	41.5	40.7
Octane CFRR-Clear	54.9	66.3	56.4	69.2	62.6	72.2
+3 cc TEL	82.2	88.7	83.3	90.7	87.5	92.4

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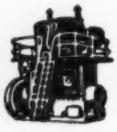

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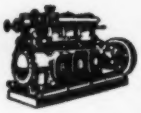

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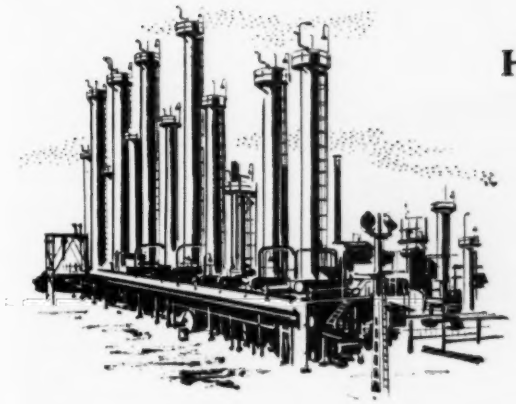

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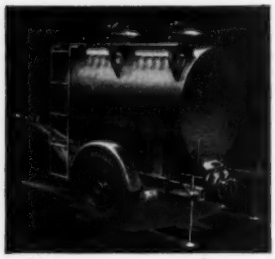

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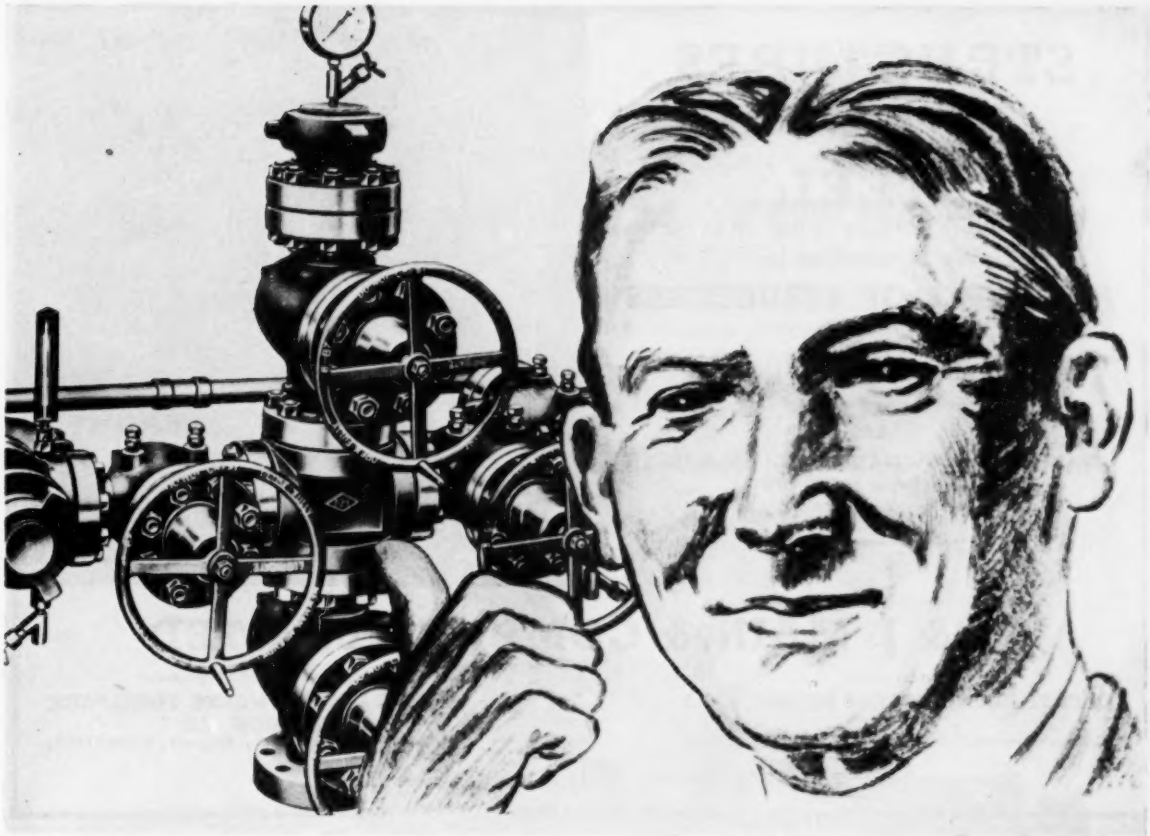

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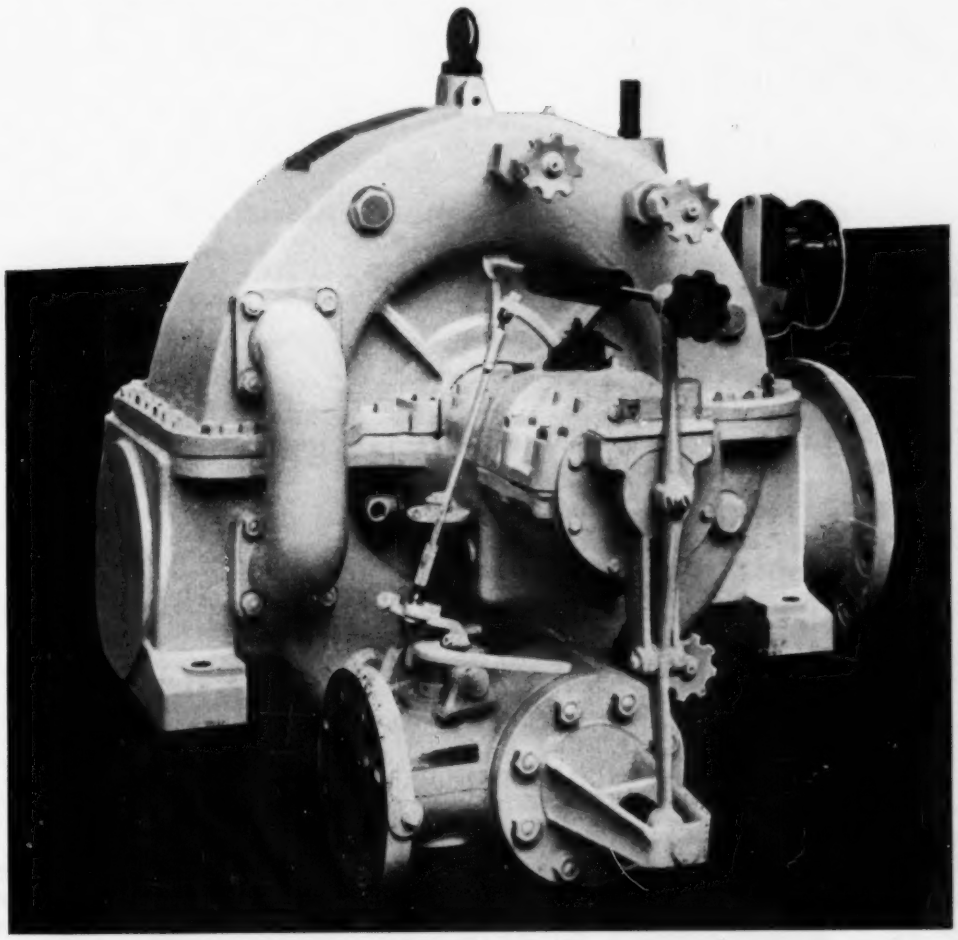

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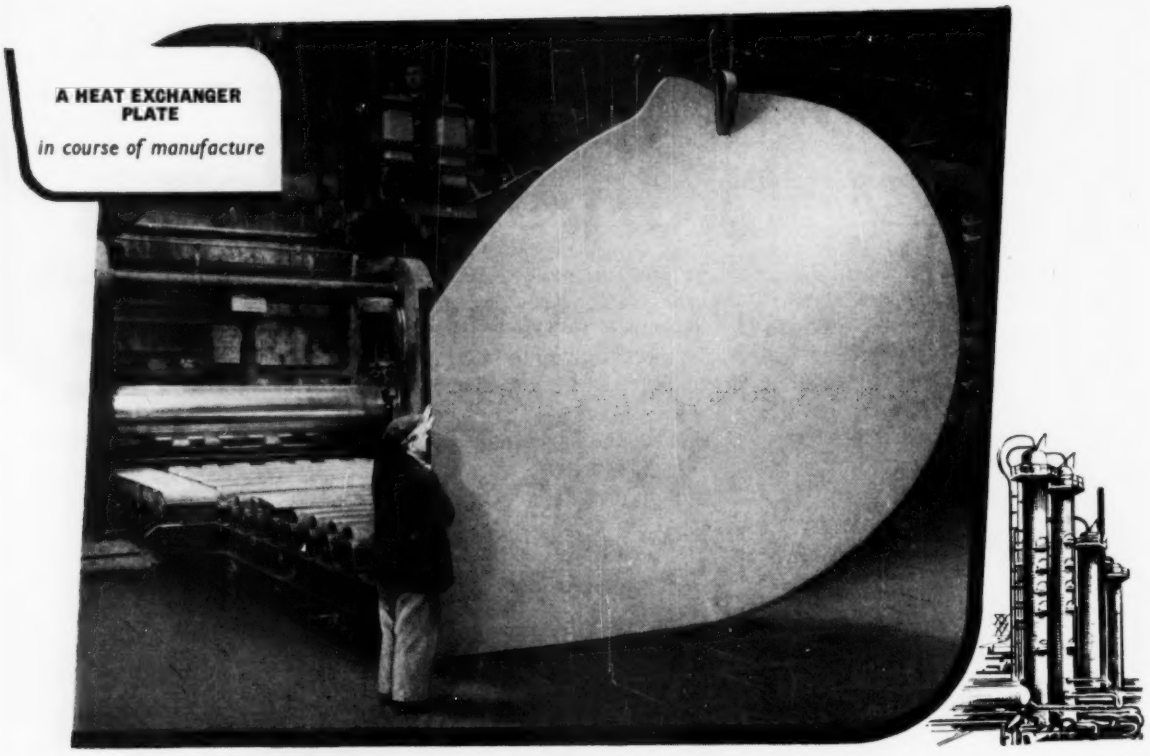

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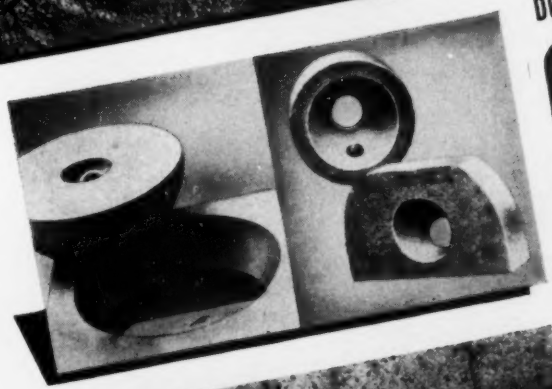

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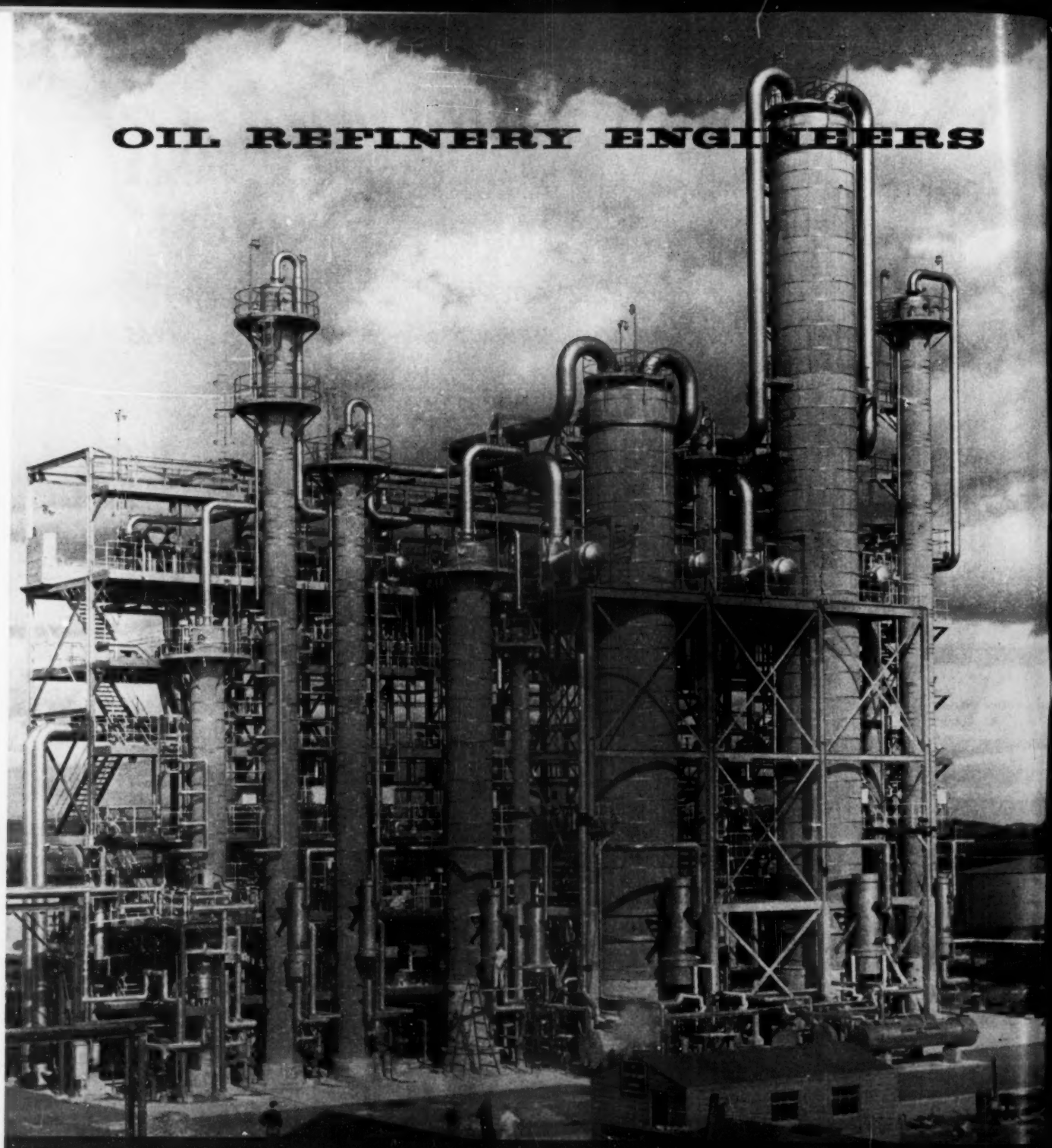

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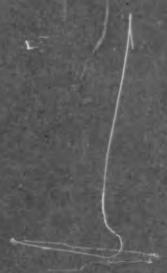

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